SYNTHESIS AND STEREOCHEMICAL STUDIES ON THE COMPLEXES OF ORGANOTINS WITH NITROGEN DONORS

ABSTRACT

THESIS SUBMITTED FOR THE DEGREE OF

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IN

Chemistry

SYED ASLAM SHAHEER

M. Sc. M. Phil.

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DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
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ABSTRACT

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The metal complexes of indazoles, imidazoles and indoles have received a greater attention in the last two decades largely because of their biological activity. Recent work in our laboratory has led to the synthesis of boron-nitrogen bonded ligands derived from indazoles, imidazoles and indoles. Complexation of these ligands have been limited only to transition metal ions. No such work seems to have been done with organotin halides. In extending our work in the tin-nitrogen chemistry area, it seemed worthwhile to carryout a study of the complexes of di- and triorganotin (IV) halides with the above mentioned ligands under this project as these studies may lead us to the discovery of some new organotin complexes of considerable structural interest which may be biologically active and may be tried as potential pesticides in agriculture.

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halides viz. ; dimethyltindichloride, dibutyltindichloride, trimethyltinchloride, tributyltinchloride and triphenyltin-chloride with several ligands containing boron-nitrogen bond, namely ; poly(nitroindazolyl)borates, poly(imidazolyl)borates, poly(2-methylimidazolyl)borates and dihydrobis(indolyl) borate, formulated as $[H_nB(In)_{4-n}]^-$ where In stand for 5, or 6-nitroindazole, imidazole, 2-methylimidazole or indole and n = 2, 1 and o, have been undertaken.

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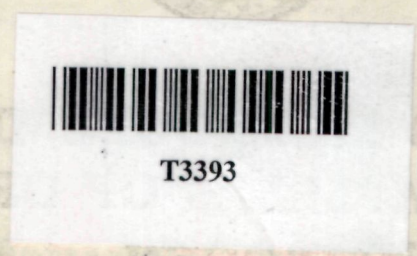
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THESIS SECTION

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TO

THE MEMORY

OF MY FATHER

Saiyid Aftab Ahmad Zaidi
M.Sc. (Alig.), M.A., Ph.D. (Toronto),
A. R. I. C. (London) F. N. A. Sc.

PROFESSOR

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Certified that the work embodied in this thesis entitled "SYNTHESIS AND STEREOCHEMICAL STUDIES ON THE COMPLEXES OF ORGANOTINS WITH NITROGEN DONORS" is the result of the original researches of Mr. Syed Aslam Shaheer, carried out under my supervision. It has not been submitted elsewhere for the award of a degree and is suitable for submission for the award of the Ph.D. degree of Aligarh Muslim University, Aligarh.

(S.A.A. Zaidi)

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PUBLICATIONS

1. Triorganotin(IV) halide complexes of Tetrakis (nitroindazolyl) borates.
   S.A.A. Zaidi, S.A. Shaheer, S.R.A. Zaidi and M. Shakir.
   Indian J. Chem., 25A, 863 (1986).

2. Organotin(IV) halide complexes of poly(imidazolyl) borates containing penta and hexacoordinated tin.
   S.A.A. Zaidi, S.A. Shaheer, S.R.A. Zaidi and T.A. Khan.
   Synth. React. Inorg. Met-org. Chem. (In press).

3. Structural studies of some penta and hexacoordinated organotin(IV) halide complexes of poly(2-methylimidazolyl) borates.
   S.A.A. Zaidi, S.A. Shaheer, S.R.A. Zaidi and T.A. Khan.
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CHAPTER I

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The field of organometallic chemistry has grown considerably in its span and variety in recent years. Organometallic compounds and their adducts now find application in such diverse fields as organic synthesis, catalytic and industrial processes, molecular biology and environmental chemistry. The organometallic chemistry, therefore, is an inter- and multi-disciplinary science of much current interest and great future potential.

The first organometallic derivative viz. diethylzinc was prepared in 1949 by Frankland. The discovery of Grignard reagent later opened a new chapter which can be entitled as the use of organometallics in organic synthesis. The discovery of Ferrocene (dicyclopentadienyliron) in 1951 appears to have provided a take off point for the synthesis of a variety of organotransition metal derivatives with a novel type of bonding, the sandwich bonding. Furthermore the discovery of a facile route for the synthesis of organoboranes via hydroboration generated more interest in this field as these compounds have proved to be much more versatile and of great utility.

The most interesting aspect of organotransition metal

chemistry is the catalytic properties of these compounds for various processes. The utilization of Ziegler-Natta catalyst in the polymerization of alkenes, alkynes and alkadienes and an understanding of the mechanism of the reactions has provided a fresh insight into the potential uses of such catalysts. These are opening new chapters in the industrial applications of organometallics which were earlier limited to use of a few derivatives like lead-tetraethyl and silicones.

The utility of organometallics in chemotherapy which was realised during the early part of this century has received continued attention. The discovery of vitamin B_{12} (containing a cobalt-carbon linkage) caused a renewed interest in bioorganometallic chemistry which has taken a new turn in recent years with the increasing awareness of the environmental aspects of metal carbon bonded compounds.

Recently developed synthesis and physico-chemical techniques has resulted into new routes for the synthesis of organometallic compounds having novel structures. Organometallic compounds of group (IV) elements in general and organotins in particular are known to possess great biological activity [1-8].

Chemistry of organometallic derivatives of tin in its

divalent state is being currently investigated with great vigour. These species are organometallic analogues of carbenes and show high reactivity.

Tin exhibits a much greater tendency to increase its coordination number from four upto eight. This has led to the preparation and isolation of a large variety of organotin complexes derived from mono-, as well as polydentate organic ligands.

Organotin halides are strong Lewis acids (the order of acid strength being $R_3SnX < R_2SnX_2 < RSnX_3$) and form addition complexes with various nitrogen and oxygen or sulphur donor bases. Triorgano-tinhalides generally yield, trigonal bipyramidal complexes whereas the di- and mono-organotinhalides form octahedral complexes. Some of the Lewis bases used recently are heterocyclic amines (e.g. pyridine, β-picoline and quinoline) urea, thiourea and 1,2-ethylenebis (diphenyl-phosphine oxide) [9,10]. Triorganotin pseudohalides (e.g. Ph_3SnX, X = NCS, NCO, NCSe and N_3) also behave as Lewis acids and form stable complexes with N, O and S donor ligands [11, 12].

Considerable amount of work has been carried out on the complexes of organotinhalides with various potentially multidentate schiff base ligands. In most of the cases for

example, $R_nSnCl_{4-n}.2L$ and $R_nSnCl_{4-n}.L$, L = $HOC_6H_4CH = NR$ and $HOC_6H_4CH = N(CH_2)_2OH$ and L = $HOC_6H_4CH = N(CH_2)_2N = CHC_6H_4OH$, octahedral complexes are formed.

Organotin halides serve as suitable starting materials for the synthesis of variety of organotin complexes containing Sn-O and Sn-S linkages. The convenient synthetic routes are nucleophilic displacement of the halogens from organotin-halides and the condensation of oxides with suitable protic reagents.

Among the various organotin chelates maximum work appears to have been carried with polydentate Schiff base ligands containing OH or SH groups in addition to imino linkage. Some of the ligands employed are N-substituted salicylaldimines, substituted benzothiazolines and those derived by the condensation of salicylaldehyde with semicarbazones, thiosemicarbazones, thiocarbonydrazide, isonicotinic acid hydrozide and alkylene diamines. Spectroscopic data indicate the presence of 5-coordinated tin in derivatives of the type $R_3SnOC_6H_4CH = NR$ and $R_2SnOC_6H_4CH = N-N-C(NH_2)-X$ (X = O or S). Similarly in the complexes of diorgano- and monoorganotin (IV) with $(HOC_6H_4CCR) = N-NH)_2C = S$ (R = H, Me), the ligands are tetradentate, the coordination of tin involves both the diprotonated phenolic oxygens,

thioamide sulphur and one of the hydrazone nitrogens. Organotin complexes of novel Schiff bases formed by condensation of O-arsanilic acids with aromatic aldehydes have been described.

Other polydentate ligands, organotin chelates of which have recently been reported are dithiazone, methyl ester of 2-amino-1-cyclopentene-1-carbodithioic acid and substituted arylarsonic acids [11]. Diorganotin arylarsonates are generally insoluble high melting solids. Based on molecular weight, IR, and Mössabauer spectral data, 5 and 6 coordinatedstructures have been postulated for these compounds.

Easy cleavage of phenyl groups attached to tin by electrophilic reagents has been utilized for the preparation of tin tetraacetate from phenyltin oxide.

The worldwide production of organotin chemicals has, over the last 25 years, risen from under 5,000 tons in 1955 to at least 30,000 tons at the present time. This increase is primarily due to wide range of industrial applications discovered for the organotin compounds and, in all probabilities tin has a larger number of its organometallic derivatives in commercial use than any other element.

On a tonnage basis, the biocidal use [2,3] of the triorganotin compounds, R_3Snx are exceeded by the non-toxic applications [12,13] of the di and mono-organotins R_2Snx_2. The tetraorganotins, R_4Sn, have no large volume of industrial outlets at the present time, being primarily used as intermediates in the manufacturing of the other types of organotin compounds, R_nSnx_{4-n} [14].

Some important advances have also been made on the toxicological aspects of organotins, particularly in connection with the chemical nature of the sites of toxic action of their compounds, the effect of molecular structure on their biological activity and finally their biochemical and environmental fate.

The organotin compounds today find use as fungicides in paper, textile and polyvinyl paint manufacture, as biocides in hospital maintenance, as heat and light stabilisers in plastic industry, as biocides in antifouling paint and timber preservation and specially as crop protectants in agriculture. The tin complexes of proteins and nucleoproteins and their hydrolysis products have been stated to be effective against certain skin and blood diseases. Dibutyltin dilaurate [15,16] is very effective remedy for certain intestinal worm infections in chickens. The rubber pellets

containing tributyltin oxide [17] are used for eradicating the snail carriers of Bilharzia. Triorganotin compounds are found to be effective against mosquitoes.

The biological activity pattern of the triorganotins, R_3Snx, shows a marked species dependence, according to the nature of R group, but relatively independent of the anionic radical X[18]. The lower trialkyl tin compounds are able to inhibit mitrochondrial phosphorylation [19, 20] and it has been suggested that their remarkable biological activity pattern may be dependent upon the effectiveness of their interaction at an active site or sites which involves coordination to certain amino acids. The trialkyl tins are indeed known to bind a number of proteins [21, 22] e.g. cat haemoglobin, rat haemoglobin, rat brain myelin, snail tissue protein etc. Aldriges recent studies [23] show that histidine residues provide one of the two binding sites for triethyltin chloride on cat and rat haemoglobin a possible point of attachment of the organotin would be via N-1 of the imidazole ring of histidine, as in the 1-triorganostannyl imidazole compounds [24].

The organotin compounds have novel use as antifeedants [25, 26]. The use of antifeedant in crop protection has several advantages over conventional techniques, the main

one being that beneficial and nontarget insects are not effected because they do not eat the treated crop. Organotin pesticides are generally compatible with other pesticides and do not harm predacious mites, insects and also honey bees. Organotin pesticides that are in current use do not accumulate in the soil with successive application. They are metabolised readily in animals and soil to inorganic tin compounds which are not taken up by plants. So, organotin pesticides, on account of their lack of accumulation and ready breakdown to non toxic inorganic tin compounds are environmentally quite acceptable [27-29].

The complexes of organotins [17, 30] have been reported to have significant biological properties and to act as pesticides. The well known pesticide Peropal (1-tricyclohexylstannyl 1,2,4-triazole) is a complex of 1,2,4-triazole.

Although the compounds containing boron-nitrogen bonds were known to exist way back in the nineteenth century [31] the chemistry of such compounds has received serious attention only in the recent years and boron-nitrogen bond has now acquired an important place as is evident from the chemical literature of the last decade. There are two interesting features in the chemistry of boron-nitrogen bond.

1. The boron-nitrogen bond is isoelectronic with

carbon-carbon single bond and

2. The sum of the covalent single bond radii of boron and nitrogen is very similar in magnitude to that of two carbon atoms.

These two features lead to some interesting analogies between certain boron nitrogen compounds and their organic counterparts. The scope of this chemistry is so wide that two books [32-33] and a number of article have recently been published [34-45].

The fertile field of boron-pyrazole chemistry [46], which includes the compounds of boron bonded to nitrogen of the pyrazole nucleus is of a great scope [47]. It has yielded novel classes of boron heterocycles, chelating ligands and transition metal compounds.

An interesting class of boron nitrogen bonded compounds of pyrazole ligand are poly (1-pyrazolyl) borates [48-50]. The parent poly (1-pyrazolyl) borate has been prepared [48] by heating an alkali metal borohydride with pyrazole. By maintaining the temperature at around 110, 180 and > 120°C respectively di-, tri- and tetra (1-pyrazolyl) borates have been obtained [51, 52]. The compound were found to be water soluble and stable to storage. They yielded

isolable, free acids on acidification [49]. The oxidative and hydrolytic stability of poly (1-pyrazolyl) borates is known to increase with decreasing number of hydrogen attached to boron [48]. Thus aqueous paramaganate instantaneously oxidized $H_2B(pz)_2^-$ while $HB(pz)_3^-$ was oxidized rather slowly and $B(pz)_4^-$ remained unaffected under these conditions.

The structure of dihydrobis (1-pyrazolyl) borate and its complexes have been based on optical spectra, magnetic and n.m.r. data [53]. The isomorphous nickel (II) and copper (II) chelates have been assigned square planar geometry whereas the chelates of manganese(II), iron (II), cobalt (II) and zinc (II) were assigned tetrahedral geometry. All these chelates were stable towards air and moisture except for the iron (II) and manganese (II). Apart from its excellent chelating ability the dihydrobis (1-pyrazolyl) borate has been found to reduce Mg (II), Ca (II), Sr (II), Ba (II), Ag (I), Pd (II) and Hg (II) to the free metals.

The hydrotris (1-pyrazolyl) borate anion is a unique example of a uninegative tridentate [52, 54] ligand. Compounds of this ligand with several divalent transition metal ions [48] have also been obtained and are reported to be trigonally distorted octahedral in structure. The transition metal compounds were all high melting solids and sublimable

in vacuo. They are sparingly soluble in polar solvents such as alcohol or acetone, but they readily dissolve in hydrocarbons and aromatic hydrocarbons.

The ligand tetrakis (1-pyrazolyl) borate anion has been found to be tridentate in almost all the cases and forms the similar type of octahedral complexes. These compounds were thermally more stable, possessed high melting points and less soluble in organic solvents than their hydrotris analogue. The solubility of these compounds were increased in aqueous minerals due to the presence of two additional pyrazolyl groups per molecule. The tetrakis anion can also act in a tetradentate fashion when pairs of N-termini are bridged by appropriate four coordinate species such as π-allyl palladium chloride [55].

The work of Trofimenko on poly (1-pyrazolyl) borate has been extended towards a new direction by Zaidi and coworkers [58-68]. They have been able to synthesize the new analogous series of dihydrobis-, hydrotris- and tetrakis- ligands by using indazoles [58-63] thiazoles [64] and imidazoles [65-68].

During the recent years the coordination chemistry of imidazoles, indazoles and indoles has assumed such

importance owing to the fact that imidazole and its substituted derivatives have been found to be of considerable biological significance. They play crucial role in the structure and functioning of a number of biologically important molecules by virtue of their being coordinated to metal ions. Literature survey reveals that although imidazole itself has a little action and is relatively non-toxic its various substituted derivatives viz, 4,5-methylimidazole, 4,5-dimethylimidazole, 4-chloroimidazole, 4-aminomethylimidazole exhibit marked physiological activity [69]. The possibility of the use of some imidazole complexes as anti tumor drug [70] has recently been reported. Imidazole is also used as an analgesic, antipyretic and anti inflammatory reagent [71]. Some metal complexes of imidazolthiol exhibit fungicidal and insecticidal activity, however, in some cases the antioxidant and heat resistant properties have also been reported [72-74]. Indazole and substituted indazoles have also been found to have antibacterial and antiinflammatory properties. 1-H indazole derivatives have been used as veterinary drug for pathological infections of respiratory organs. Some indazole derivatives have been found to be plant growth regulators.

As a result of biological activities and also as a part of general interest, the chemistry of the metal complexes

of imidazoles, indazoles and indoles have received great attention in recent years [75-93]. The studies so far carried on imidazoles, indazoles and indoles for the synthesis of chelating ligands where boron is bonded to the nitrogen atom of the imidazole, indazole or indole nucleus are limited only to transition metals. However, such work does not seem to have been done on organotin (IV) halides. It is, therefore considered worthwhile to undertake the study of the complexes of di- and triorganotin (IV) halide with the above ligands under this project.

Although there is a good deal of work on the toxic behaviour of organotins, only a few complexes of organotins have been reported to have biological activity. These studies will lead us to search new complexes of organotins which may be biologically active and subsequently may be used as pesticides to eradicate various diseases in agriculture crops.

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CHAPTER II

EXPERIMENTAL METHODS

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EXPERIMENTAL METHODS

Several physico-chemical methods are available now-a-days for structure elucidation of coordination compounds. The techniques used for the investigation of the presently synthesized compounds described in this work are as follows :

1. Infrared spectroscopy
2. Nuclear magnetic resonance spectroscopy
3. Molar conductance measurements
4. Elemental analysis

A brief discussion of these methods will be appropriate and is given below.

1. Infrared spectroscopy

The feature of characteristic absorption of radiation by many molecules in infrared (IR) region has provided physicists and chemists with an extremely elegant and powerful tool for the elucidation of molecular structure. The infrared region has been classified into three categories : near IR, 0.8 to 2.5 μ (12,500 to 4000 cm^{-1}), IR, 2.5 to 15 μ (4000 to 667 cm^{-1}) and for IR, 15 to 200 μ (667 to 50 cm^{-1}).

Infrared spectrum arises from the different modes of vibrations and rotation in a molecule. The pure rotational

spectrum of molecules occurs at a very long wave length limit of about 25 μ. At wave length below 25 μ the radiation has sufficient energy to cause changes in the vibrational and of course of the rotational level of molecule.

According to the quantum theory there are discrete energy states, both rotational and vibrational in which each molecule can exist. For diatomic, linear poly atomic and spherical top molecules the energy of rotational levels is given by the equation ;

$$E_r = \frac{J\,(J+1)\,h^2}{8\,\pi^2\,I} \qquad (1)$$

where J is rotational quantum number which can have any integral value 0, 1, 2, 3 and I is the moment of inertia of the molecule above the axis of rotation.

For the symmetrical and asymmetrical molecules the formula is somewhat more complex. Transitions between the different rotational levels in the microwave and infrared regions are governed by the selection rules.

$$\Delta J = \pm 1$$

If a molecule is raised from an energy state with a quantum number J+1, the energy involved will be

$$h\nu = \Delta E = E_{(J+1)} - E_J \qquad (2)$$

from which the frequency of energy absorbed in wavenumber can be obtained by substitution of equation (1) in equation (2) as follows

$$\nu_r = \frac{h(J+1)}{4\pi^2 IC} = 2B\,(J+1) \qquad (3)$$

where B, the rotational constant, is equal to $h/8\,\pi^2 IC$. The pure rotational spectrum then would consist of equally spaced lines. The constant frequency separation between successive lines being equal to 2B, i.e. to $h/4\,\pi^2\,IC\ cm^{-1}$. It is observed that as the moment of inertia I increases, the frequency of the rotational lines for a given I value, decreases. For relatively heavy or large molecules, the pure rotational spectrum will thus appear in the very far infrared region.

In the infrared region below 25 μ changes in the vibrational states of the molecule occur during absorption of radiation for small amplitude of vibration, the vibration may be considered harmonic and the energy of the vibrational quantum level is given by eqn. (4).

$$E_V = h\omega\,(V + 1/2) \qquad (4)$$

where ω is the fundamental vibrational frequency of the

harmonic oscillator and V is the vibrational quantum number which can have any integral value 0, 1, 2, 3 .... The difference in energy between successive energy levels of the harmonic oscillator is thus always $h\omega$.

In order that a vibrating molecule should interact with the fluctuating electrical field of electromagnetic radiation the molecular electrical dipole moment must change its magnitude or orientation with respect to a coordinate system during the motion. It is the magnitude of the change of dipole moment which determines the intensity of a transition. There are 3N-6 normal vibrations of a nonlinear molecule of N atom and hence the 3N-6 frequencies associated with them are called fundamental frequencies of a molecule. From a symmetry that a molecule possesses one can determine how many of the 3N-6 vibrations will be observed in its infrared spectrum and conversely from the infrared spectrum the molecular symmetry may be deduced. A vibration will be infrared active if its symmetry species is the same as that of at least one of the dipole moment components. For harmonic oscillators, transitions between the various energy levels are governed by the selection rule $\Delta V = \pm 1$. In actual fact, the purely harmonic conditions do not prevail for real molecules. The frequent observation of overtones and combination tones of these vibration corresponding to change

$\Delta V = 2,3$ etc. is a consequence of the anharmonic nature of the normal modes. These additional bands are usually very much weaker than the parent fundamentals.

For harmonic oscillation of frequency is related to the force 'f' binding the vibrating groups together and the reduced mass μ, by the relationship

$$2\pi\omega = (f/\mu)^{1/2}, \quad \mu = \frac{m_A m_B}{m_B + m_B} \tag{5}$$

where m_A and m_B are the masses attached to either of the vibrating system. In terms of the frequency ν_v, in wave numbers, eqn. (5) becomes

$$\nu_v = \frac{1}{2\pi C}\sqrt{f/\mu} \tag{6}$$

Thus the frequencies of vibration of a molecule are related to the masses and binding forces. In many of the normal modes of vibrations of a molecule the main participants in the vibration are two atoms held together by a chemical bond. The frequencies are only slightly affected by another atom attached to the atoms, concerned, and thus these vibrational modes are characteristic of the group in the molecule and are very useful in identifying a compound.

In this work only those frequencies which are pertinent

to the structure elucidation of the newly synthesized compounds will be discussed.

N-H stretching vibrations

The N-H stretching vibrations occur in the region 3500-3300 cm^{-1} in dilute solutions [1]. Primary amines in dilute solutions of non-polar solvents give two absorption bands in this region. The first which is due to symmetric stretch is usually found near 3500 cm^{-1} and second which arises from corresponding asymmetrical mode is found near 3400 cm^{-1}. The position and intensity of both these bands are sensitive to substitution. Secondary amines show only a single N-H stretching absorption in dilute solution in the above mentioned region. The intensity and frequency of N-H stretching vibrations of secondary amines are very sensitive to structural changes. The band is found in the range 3350-3310 cm^{-1} (low intensity) in aliphatic secondary amines and near 3490 cm^{-1} (much higher intensity) in hterocyclic secondary amines such as pyrole and indoles.

The N-H stretching absorption shifts to lower values in the solid state due to extensive hydrogen bonding. At a very low concentration pyrolidine shows a band at 3367 cm^{-1} due to the monomeric N-H stretching frequency[2]. As the

concentration increases, a new band appears at 3268 cm^{-1} due to intermolecular association (N-H——N bonding). The intensity of the low frequency band increases with increasing concentration until complete association occurs in the liquid state. The OH stretching frequencies are observed over about the same range as NH frequencies. Except for free N-H stretching, the observed absorption of an NH is normally lower than that for OH. This is a useful means of distinguishing between NH and OH mode.

C-H stretching vibrations

These vibrations are usually observed in the 3100-3000 cm^{-1} region in carbocyclic and heterocyclic systems [2]. Some aromatic compounds give rise to three bands near 3038 cm^{-1} region. The position of C-H stretching vibrations are among the most stable in the spectrum. A large number of saturated hydrocarbons containing methyl group shows [4] two distinct bands at 2960 cm^{-1} and 2870 cm^{-1} in all the cases. The first of these results from the asymmetric mode in which two C-H band of the methyl group are extending while the third one is contracting (ν_{as} CH_3). The second arises from symmetric stretching ($\nu_s CH_3$) in which all three of the C-H bonds extend and contract in phase. The presence of several

methyl groups in a molecule results in strong absorption bands at these positions.

C=N stretching vibrations

A band of variable intensity in the region 1690-1640 cm^{-1} is attributed to C=N stretching vibrations in an open-chain system or in a non-conjugated ring system [5]. With conjugated cyclic systems the position is much less clear and the C=N absorptions have been assigned as being within the range 1660-1480 cm^{-1}. In cyclic compounds and incyclic compounds without internal conjugation the C=N absorption is assigned to the 1650 cm^{-1} region. The C=N absorption band occurs near 1667 cm^{-1} region in oxazines, oxazolines, oximes and imines. However, the C=N absorption bands are difficult to identify for two reasons. First owing to the considerable changes in intensity which follow changes in its environment, and secondary because information available on the effects of conjugation in ring system is often conflicting and indecisive.

Ring stretching vibrations

Aromatic ring stretching vibrations appear in the region 1600-1350 cm^{-1} in most of the heterocyclic compounds [2]. The position and intensity of these vibrations are dependent on the nature of the ring and type of substitution.

Six membered ring shows four bands at around 1605, 1575, 1480 and 1430 cm^{-1}, whereas five membered rings show these bands at around 1590, 1490 and 1400 cm^{-1}. The intensities of these bands give an idea of the patterns and nature of substitution in the ring.

The characteristic pattern of absorption of the ring stretching vibrations result from the complete interaction of the C=C, C=N and or N=N vibrations (e.g. in 1,2-diazine) and it is, therefore very difficult to isolate the different vibrations. This is due to the fact that the lone pair of electron on the nitrogen atom will be able to conjugate with the ring, the magnitude of which depends on the coplanarity of the system. Therefore these vibrations are sensitive to minor alterations in molecular geometry and are difficult to distinguish from other vibrations.

B-H stretching vibrations

The B-H stretching frequencies generally appear as a band in the 2450-2300 cm^{-1} region in the transition metal borohydrides [6]. The B-H stretching frequency in decaborane occurs at 2580 cm^{-1} and B-H skeletal vibration at 1008 cm^{-1} [7]. In poly (1 pyrazolyl) borate [8] the B-H stretching frequency has been found in the range 2470-2240 cm^{-1} either in the form of a sharp band of medium intensity or as a broad multiplet.

B-N stretching vibrations

The vibration frequencies of B-N bands are found in diaminoborane. A ν_{as} B-N stretching band at 1605 or 1393 cm^{-1} is seen in the infrared spectra [9].

Metal-halogen vibrations

Metal halogen vibrations which appear in the low frequency infrared region, are quite useful in determining the stereochemistry of coordination compounds. In a tetrahedral MX_4 molecule (T_d) there are four normal modes of vibration. All the four vibrations are Raman active, whereas only two (ν_3, ν_4) are infrared active, and their position depends upon the mass of the metal and halogen [10]. For an octahedral MX_6 molecule (O_h) (e.g. $GeCl_6^{-2}$, Sn_6^{-2} etc.) there are six possible normal modes of vibration. Three (ν_1, ν_2 and ν_5) are Raman active whereas only two (ν_3, ν_4) are infrared active [11]. In octahedral ions (GeX_6^{-2}, SnX_6^{-2} etc.) the M-X vibrations are found at lower frequencies than those found for similar vibrations in a tetrahedral environment. In many addition compounds metal halogen vibrations are much more intensive than ligand vibrations. In group IV, this is most marked for adducts in the tin tetrahalides and least marked for adducts of silicon tetrahalides where intensities are frequently comparable. Ligands may occupy

either a cis or a trans positions in the octahedron. The use of infrared spectroscopy in the far IR region to study the cis trans isomerism of the adducts of type MX_4, L_2 (where M=tin, silicon or germinium, X is halogen and L is a monodentate ligand) has been outlined by many workers [13-22].

Beattie and co-workers [23] carried out a normal coordinate analysis of the octahedral species cis and trans MX_4, L_2 by Wilsons F-G matrix method, and calculated vibrational frequencies for coordination compounds of some tetrahalides of group (IV). The calculation shows that for a cis-adduct three high frequency bands are expected, the next nearest band lying considerably below this group (all the bands are infrared and Raman active). In case of the trans adducts if the metal-ligand force constant is low compared with the metal halogen there will be one main band in the same region as the set of three absorptions mentioned for the cis-adducts. However, where the metal ligand force constant is high, the e_u and a_{2u} vibrations (both IR active) will occur in similar regions of the spectrum. Thus in a crystalline compound, crystal field resolution of a e_u vibration to doublet, plus the presence of an a_{2u} vibration could lead to a spectrum similar to that of a cis-adduct. The e_u vibration (anti symmetric stretch)

is relatively insensitive to the value of f_{M-L} and also to the value of the bending force constants. Thus, identification of cis- and trans- isomers by infrared spectroscopic examination is helpful in favourable cases, particularly when solution spectra can be obtained.

Metal-carbon stretching frequencies

IR spectroscopy is quite valuable as it provides information on the configuration of organotin compounds. Particularly important criterion established for determining the configuration of SnC_3 and SnC_2 moieties in trimethyl tin and dimethyl tin derivatives [24]. If the spectrum reveals two Sn-C stretching vibrations (both the symmetric and the asymmetric modes), the configuration of SnC_3 group is non planar or that of SnC_2 is non linear. However, if there is only one band assignable to an Sn-C stretching vibration, the configuration of SnC_3 group is planar or that of SnC_2 is linear [25]. This criterion has been further supported by X-ray studies.

Metal nitrogen stretching frequencies

The metal-nitrogen stretching frequencies are of particular interest since it leads to direct information regarding the coordinate bond [26]. The infrared spectra of pyridine complexes in 200-700 cm^{-1} region shows bands which

were assigned to M-N vibrations [27]. Several amines complexes [28,29] exhibited the metal nitrogen frequency band in the region 300-420 cm^{-1}. The bands obtained in the region 150-350 cm^{-1} in several metal derivatives of imidazole has, however, been assigned to the M-N stretching frequency.

2. Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectrometry is basically another form of absorption spectrometry. Under appropriate conditions a sample can absorb electromagnetic radiation in the radio frequency region at frequencies governed by the characteristics of the sample. Absorption is a function of certain nuclei in the molecule. A plot of the frequencies of the absorption peaks versus peak intensities constitutes an NMR spectrum. All forms of spectroscopy give spectra that may be described in terms of frequency, intensity and shape of spectral lines or bands. These observable properties depend on molecular parameters of the system, which for NMR are found to be the shielding constants and coupling constant of the nuclei, and the lifetimes of energy levels. It is these parameters which are of fundamental physicochemical importance. The NMR spectroscopy is concerned with (a) obtaining spectra (b) evaluating the nuclear magnetic

parameters from the spectra (c) interpreting or predicting these parameters using physical or theoretical models and (d) applying the knowledge gained to problems of chemical interest such as structure determination.

Two properties of nuclear particles pertinent to an understanding of nuclear magnetic resonance spectroscopy are the net spin associated with the protons and neutrons (both have a spin quantum number 1/2) and the distribution of position of positive charge. All nuclei carry a charge. In some nuclei this charge circulates or spins on the nuclear axis, and this circulation of nuclear charge generates a magnetic dipole along the axis. The angular momentum of the spinning charge can be described in terms of spin quantum number I, these numbers have values of 0, 1/2, 1, 3/2 and so forth. (I=0 has no spin). The intrinsic magnitude of generated dipole is expressed in terms of a nuclear magnetic moment μ.

In general, nuclei with an even number of protons and an even number of neutrons have a spin quantum number I of zero. Both C^{12} and O^{16} fall in this category, they do not give rise to an NMR signal or interfere with a proton NMR signal.

Several nuclei (H^1, F^{19}, C^{13} and P^{31}) have spin number 1 or 1/2. These nuclei possess a uniform spherical charge

distribution and are characterized by having either an odd number of protons or an odd number of neutrons.

Nuclei with spin quantum number I of 1 or higher have a nonspherical charge distribution, this asymmetry is described by an electrical quadrupole moment which, as effect the relaxation time and thus the coupling with neighbouring nuclei. N^{14} and H^{2} have spin number I of 1. B^{11}, Cl^{35}, Cl^{37}, Br^{79} and Br^{81} are examples of nuclei with N = 3/2.

The spin quantum number I determines the number of orientation a nucleus may assume in an external uniform magnetic field in accordance with the formula 2 I + 1. Here, we are concerned with the proton whose spin number I is 1/2. Thus, the proton has two orientations in an applied uniform magnetic field parallel with the applied field (aligned with the field) or antiparallel (aligned against the field). The former is low energy (stable) state, the latter, the high energy (unstable) state. The energy levels are a function of the magnitude of the nuclear magnetic moment μ and the strength of the applied external magnetic field, Ho.

Two energy levels for the proton having been established, it should now be possible to introduce quanta of energy, $h\nu$ (h is Planck's constant, ν is frequency of electromagnetic radiation) such that the parallel orientation (low energy

state) can be flipped to the antiparallel (high energy state) in a magnetic field of given strength Ho. The fundamental NMR equation correlating electromagnetic frequency with magnetic field strength is

$$\nu = \gamma \, Ho/2\pi$$

The constant γ is called the magnetogyric ratio and is a fundamental nuclear constant.

The problem now is how to inject electromagnetic energy into proton aligned in a magnetic field so as to flip the proton spin into a higher energy level and how to measure the energy thus obtained. We consider one peculiarity of a small magnet spinning in an external magnetic field. The axis of small magnet (the proton) will precess about the axis of the external magnetic field in the same manner in which a spinning gyroscope precesses under the influence of gravity. The precessional angular velocity ω_o is equal to the product of the magnetogyric ratio, γ and the strength of the applied magnetic field Ho

$$\omega_o = \gamma \, Ho$$

by recalling the fundamental NMR equation that

$$\gamma \, Ho = 2\pi\nu$$

Therefore

$$\omega_o = 2\ \pi\nu$$

This means the if we can introduce the same frequency equal to γHo i.e. Larmour frequency (the energy require to flip a proton), we shall be precisely attuned to the precessional angular velocity or the inserted frequency will be in resonance with the precessional frequency. The energy of inserted frequency can thus be absorbed by the nucleus and given tne proper geometry, the nucleus can be caused to flip. This involves a frequency of 60 megacycles per second at the magnetic field Ho of 14,092 gauss for the proton (or any other desired combination in the same ratio).

Now we subject the protons to a powerful uniform magnetic field. The protons are now aligned parallel with the field and are precessing about tne axis of the applied magnetic field. The electromagnetic frequency is applied in such a way that its magnetic component H_1 is at right angle to the main magnetic field Ho and is rotating with the precessing proton. An oscillator coil whose axis is at right angle to the main magnetic field Ho and will generate a linear oscillating magnetic field H_1 along the direction of the coil axis. A linear oscillating magnetic field can be resolved into two components rotating in opposite directions. One of the components is rotating in the same

direction as the precessional orbit of the nuclear magnetic dipole (the proton) the oppositely rotating component of H_1 is disregarded. If Ho is held constant and the oscillator frequency is increased, the angular velocity of the component of rotating magnetic field H_1 will increase until it is equal to (in resonance with) the angular velocity ω_o of the precessing proton. At this point, energy is absorbed, the nucleus flips to its higher energy level, and the recorder shows a peak. In actual practice, the oscillator frequency is constant and Ho is swept over a narrow range. Now we need some mechanism to return the nucleus to its lower energy state. In the absence of such a mechanism all of the small excess population of nuclei in the lower energy state will be raised to higher energy state and no more energy will be absorbed. There is a mechanism in which the nucleus in the higher energy state can lose energy to its environment and thus return to its lower energy state. The mechanism is called spin-lattice, or longitudinal relaxation process and involves transfer of energy from the nucleus in its high energy state to the molecular lattice. Its efficiency is described as the line T_1 taken for the transfer. An efficient relaxation process involves a short time T_1 and results in broadening of the absorption peak. In liquids and gases, the time T_1 is of the proper duration to produce a peak of usable width.

Position of signals (Chemical Shift)

The NMR phenomenon has significance to the chemist because the energy of the resonance is dependent upon the electronic environment about the nucleus. The electrons shield the nucleus so that the magnitude of the field seen at the nucleus H_N is different from the applied field Ho

$$H_N = Ho\ (1 - \sigma) \qquad (1)$$

where σ, the shielding constant, is a dimensionless quantity which represents the shielding of the nucleus by the electrons. The value of the shielding constant, σ, depends on several factors, among which are the hybridization and electronegativity of the groups attached to the atom containing the nucleus being studied.

The next concern is to calibrate the horizontal axis so that the field strength (or some function of it) at which the protons absorb energy from the radiofrequency probe can be recorded. The equation 1 can be employed, but accurate measurement of H_N and Ho is difficult. Instead, a reference material is employed and the difference between the field strength at which the sample nucleus and the nucleus in the reference compound absorbs is measured. For a given probe the field experienced by the nucleus that is necessary for any proton to undergo resonance, H, is a constant. According

to equation 1, the applied field necessary to cause the sample and reference protons to undergo resonance, H_S and H_R, respectively, is given by

$$H_S - H_R = Ho\ (\sigma_R - \sigma_S)$$

$$H = H_S\ (1 - \sigma_S) \text{ and } H = H_R\ (1 - \sigma_R)$$

where σ_S and σ_R are the shielding constants for the sample and reference.

Consequently

$$H_S\ (1 - \sigma_S) = H_R\ (1 - \sigma_R)$$

or

$$\frac{1 - \sigma_R}{1 - \sigma_S} = \frac{H_S}{H_R}$$

substracting one from both sides and rearranging, one obtained

$$\frac{\sigma_S - \sigma_R}{1 - \sigma_S} = \frac{H_S - H_R}{H_R} \qquad (2)$$

since σ_S <<< 1, equation 2 becomes

$$\delta = \sigma_S - \sigma_R = \frac{H_S - H_R}{H_R}$$

where δ, the chemical shift, is defined as the difference in

the shielding constants of the sample and reference. The relationship between H and frequency in cps is given by $V = \gamma H/2\pi$. Since the separation of the reference and sample signals is often measured in units of frequency (cps), the above equation for δ is more conveniently written as

$$\delta = \sigma_S - \sigma_R = \frac{V_S - V_R}{V_R} \qquad (3)$$

The quantities V_R and V_S are very large numbers which are only slightly different than V_o, the fixed frequency of the prob (commonly 40 or 60 m sec^{-1} for protons). As a result equation 3 can be written as

$$\delta = \frac{V_S - V_R}{V_o} \qquad (4)$$

The quantity δ is referred to as the chemical shift. The quantity $V_S - V_R$, the difference between the resonance frequencies of the sample and reference is often referred to by the symbol Δ. The quantity ν_o refers to the constant probe frequency employed. Δ depends upon the nature of the number of cycle/sec. i.e. the frequency. It is required that the rate at which the field changes be constant. The quantity δ is calculated from Δ by the use of equation 4.

$$\delta = \frac{\Delta \times 10^6}{\text{fixed frequency of probe } \nu_o}$$

therefore

$$\delta = \frac{\nu_S - \nu_R}{\nu_o} \times 10^6$$

The frequency of commonly employed probe for proton is 60000000 cps (i.e. 60 mc sec^{-1}). The factor 10^6 employed in equation 4 to give convenient number for δ in unit of part per million.

Spin-spin splitting

This can be described as the indirect coupling of protons spin through the intervening bonding electrons. Very briefly, it occurs because there is some tendency for a bonding electron to pair its spin with the spin of the nearest proton, the spin of a bonding electron having been influenced, this electron will affect the spin of the other bonding electron and so on through to the next proton. If the two protons are in very different chemical environment from one another, each will give rise to a peak depending on its chemical shift and the peaks will be quite widely separated. But the spin of each proton is affected slightly by the other proton in two ways through the intervening electrons so that each peak appears as a doublet under good resolution. The distance between the peaks of a doublet is proportional to the effectiveness of the coupling and is donated by a coupling constant J. The parameter is usually expressed in

cycle per second.

There have been many applications of spin-spin coupling to determination of structures.

Protons attached to metal ions are generally very highly shielded, the resonance often occuring 10 to 20 ppm on the high field side of the water peak (which lies about 5 ppm to the low field side of TMS). The metal atoms give rise to local environments of high diamagnetic shielding. It has been concluded that the shielding can be attributed to the electron density on H from nonpolar nature of the M-H bond and from shielding resulting from electron density in the large and diffuse 4_S and 4_p levels of the metal.

The nature of the spectra of complex molecules depends on the number of bonds through which spin-spin coupling can be transmitted. For proton proton coupling in saturated molecules of the light element, the magnitude of J falls off rapidly as the number of bonds between the two nuclei increases and usually is negligible for coupling of nuclei separated by more than three bonds. Long range coupling (coupling over more than three bonds) is often observed in unsaturated molecules.

When spin spin coupling involves an atom other than hydrogen long range coupling can occur by a mechanism

different from through space coupling. This interaction is again one of spin polarization, but it occurs through non-bonding pairs of electrons, and the coupling is through space instead of through σ or π bonds.

If the two nuclei splitting another group in a molecule are magnetically nonequivalent, the spectrum will be very much different from that in which there is splitting by two like nuclei. Four lines of equal intensity will result from splitting by two nonequivalent nuclei with $I = 1/2$ and three lines with an intensity ratio 1:2:1 will be observed for splitting by two equivalent nuclei.

3. Molar conductance

The conductivity measurement is the simplest and most easily available technique for the characterization of compounds. It gives direct information regarding whether a given complex is ionic or covalent. Several studies of molar conductivities [30-42] of different kind of electrolytes in different solvents are now available and it is useful to compare molar conductance (Λ_m) value of a given complex with that of similar electrolyte. Conventionally solution of 10^{-3} M strength is used for the conductance measurements. Molar conductance values for different types of electrolytes in nitrobenzene at this concentration are as 1:1,

20-30, 2:1, 50-60 ohm^{-1} cm^2 $mole^{-1}$. Similarly, a 1:1 electrolyte may have a value of 50-75 ohm^{-1} cm^2 $mole^{-1}$ in DMSO, 65-90 ohm^{-1} cm^2 $mole^{-1}$ in DMF, 80-115 ohm^{-1} cm^2 $mole^{-1}$ in methanol and a solution of 2:1 electrolyte may have a value of 130-170 ohm^{-1} cm^2 $mole^{-1}$ in DMF and 160-220 ohm^{-1} cm^2 $mole^{-1}$ in methanol.

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C H A P T E R III

SYNTHESIS AND CHARACTERIZATION OF THE COMPLEXES OF DI- AND TRI ORGANOTIN (IV) HALIDE WITH POLY (NITROINDAZOLYL) BORATE ANIONS

CHAPTER III

SYNTHESIS AND CHARACTERIZATION OF THE COMPLEXES OF DI- AND TRIORGANOTIN (IV) HALIDE WITH POLY (NITROINDAZOLYL) BORATE ANIONS

INTRODUCTION

Chelating agents having boron-nitrogen bond have recently been the subject of extensive research pursuit by coordination chemists. An interesting series of such ligands are poly (1-pyrazolyl) borates [1] which have been synthesized by gradually replacing the hydrogen atoms of the borohydride moiety by the pyrazole molecules in the molten condition. This has provided a new route to the synthesis of various other similar ligands involving indazole, a ligand having essentially the same basic reactive structure. The importance of this synthesis is that it orients these nitrogen containing heterocycles tetrahedrally around the boron atom, thus providing ligands with various symmetry groups. Recently in our laboratory work has been successfully carried out with indazoles and substituted indazoles [2-5]. The above mentioned ligands have been shown to be very suitable chelating agents towards a number of first row transition metal ions yielding some interesting complexes. However, their complexes with di- and trialkyltinhalides are still unknown. It, therefore, seemed interesting to undertake the study of the complexes of

di- and triorganotin (IV) halides with poly (nitroindazolyl) borate anions with a view to examining their coordinating ability towards the tin atom and also to observe the effect of the presence of the nitro- group upon chelating behaviour of these ligands, if any.

EXPERIMENTAL

Dibutyltindichloride, dimethyltindichloride, tributyltinchloride, trimethyltinchloride and triphenyltinchloride were procured from E. Merck and Fluka, 5-nitroindazole, 6-nitroindazole from Koch-Light and potassium borohydride from BDH. The solvents were dried and distilled by conventional methods.

Preparation of the Ligands

Potassium dihydrobis (5-nitroindazolyl) borate

Potassium borohydride 0.33 g (6.0 mmol) and 5-nitroindazole 2 g (12.0 mmol) were mixed together and transferred into the refluxing flask containing 30 ml of dry DMF. The solid materials were dissolved by gently shaking the refluxing flask. This solution was refluxed until 12.0 mmol hydrogen gas was collected over water. The reaction was brisk in the beginning but slackened up near completion. The whole process may be represented as :

$$KBH_4 + 2C_7H_5N_3O_2 \rightarrow K^+[C_{14}H_{10}N_6BO_4]^- + 2H_2$$

The resulting solution was concentrated to about half of its original volume by heating on a water bath. The solution yielded only about 10 mg of crystals on standing for about two months. Other methods for recrystallization tried with a view to increasing the yield of the product did not prove to be effective. The poor yield of the crystals from DMF solution suggested direct use of the salt solution for complexation.

Potassium hydrotris (5-nitroindazolyl) borate

To a thoroughly ground mixture of potassium borohydride 0.11 g (2.0 mmol) and 5-nitroindazole 1.0 g (6.0 mmol) taken in a refluxing flask 30 ml of DMF was added. The reaction started in cold. The reaction was run at reflux by slowly heating the contents of the flask causing a brisk evolution of hydrogen gas. Heating was intensified later and the flask gently shaken from time to time to promote the reaction rate. The reaction was stopped when 6.0 mmol of hydrogen gas was collected ($\sim$ 24 hour) according to the following reaction :

$$KBH_4 + 3C_7H_5N_3O_2 \rightarrow K^+[C_{21}H_{13}N_9BO_6]^- + 3H_2$$

This solution did not yield any isolable solid material even

on keeping for a long time after concentration as was done for the dihydrobis ligand. When DMF was evaporated from this solution, a viscous mass was obtained. Further drying of this mass caused decomposition of the product. The viscous mass was soluble in ether and acetone but it failed to crystallize out of these solvents. Because of these difficulties it was decided to use the solution as such for complexation.

Potassium tetrakis (5-nitroindazolyl) borate

A powdered potassium borohydride 0.08 g (1.5 mmol) and 5 nitroindazole 1.0 g (6.0 mmol) was dissolved in 50 ml of dry DMF by gently shaking the contents of the flask and refluxing for about forty eight hours. In the beginning a slow heating was required. However, intense heating was required when the reaction was near completion as it became very sluggish. The whole reaction can be summarised as :

$$KBH_4 + 4C_7H_5N_3O_2 \rightarrow K^+[C_{28}H_{16}N_{12}BO_8]^- + 4H_2$$

It was not possible to get solid material from this solution even on keeping for prolonged period for recrystallization. Removal of DMF tended to give a tar like mass, hence the solution containing the ligand was used as such for complexation.

Potassium dihydrobis (6-nitroindazolyl) borate

Powdered potassium borohydride 0.33 g (6.0 mmol) and 6-nitroindazole 2.09 g (12.0 mmol) were mixed together and dissolved in 20 ml of dry DMF in a refluxing flask. The mixture was completely dissolved by gently shaking the flask. The reaction was brisk as soon as the refluxing was started and at that moment very slow heating was done. The heating was intensified after a few hours in order to increase the rate of reaction. The refluxing was carried out for about twelve hours until 12.0 mmol of hydrogen gas was evolved. The reaction may be represented as :

$$KBH_4 + 2C_7H_5N_3O_2 \rightarrow K^+[C_{14}H_{10}N_6BO_4]^- + 2H_2$$

The resulting solution was concentrated to half of its volume by heating it on water bath. The solution yielded about 7 mg of crystals on standing for about two months. Owing to the poor yield, the salt solution had to be directly used for complexation.

Potassium hydrotris (6-nitroindazolyl) borate

Potassium borohydride 0.11 g (2.0 mmol) and 6 nitro-indazole 1 g (6.0 mmol) were mixed together in a mortar and transferred into a refluxing flask. Addition of 30 ml of

dry DMF to the contents of the flask started the reaction. The resulting solution was refluxed for about twenty four hours during which (6.0 mmol) of hydrogen gas was evolved, i.e.

$$KBH_4 + 3C_7H_5N_3O_2 \rightarrow K^+[C_{21}H_{13}N_9BO_6]^- + 3H_2$$

It was not possible to isolate any solid material from this finally obtained solution. Evaporation of the DMF led to a viscous mass which on further heating tended to explode. Complexation was,therefore,carried out from the above ligand solution.

Potassium tetrakis (6-nitroindazolyl) borate

A mixture of potassium borohydride 0.08 g (1.5 mmol) and 6 nitroindazole 1.0 g (6.0 mmol) were ground together and taken in a refluxing flask. The reaction was started as soon as 50 ml of dry DMF was added into the contents. The constituents of the mixture were totally dissolved by shaking the flask gently. A slow evolution of hydrogen gas was turned into a brisk liberation when refluxing was started. The reaction gradually subsided with a slower rate of evolution of hydrogen gas. The refluxing was continued for approximately forty eight hours until 12.0 mmol of hydrogen gas was evolved i.e.

$$KBH_4 + 4C_7H_5N_3O_2 \rightarrow K^+[C_{28}H_{16}N_{12}BO_8]^- + 4H_2$$

No solid product could be isolated. Evaporation of DMF gave a stricky tar like mass which could not be dried and the salt solution as such was therefore used for complexation.

Preparation of the complexes

Dihydrobis (5-nitroindazolyl) borate complexes

An ice cold solution of dihydrobis (5-nitroindazolyl) borate was added in the solutions of dibutyltindichloride 1 g (3.29 mmol), dimethyltindichloride 1 g (4.55 mmol), tributyltinchloride 1 g (3.08 mmol), trimethyltinchloride 1 g (5.01 mmol) or triphenyltinchloride 1 g (2.59 mmol) in ethanol (~ 25 ml) and the resulting solution was stirred for about 6 hours. The temperature of the reaction mixtures was maintained at 0^oC. After the removal of the precipitated KCl, a yellowish white products was obtained after about a weeks time. These were then filtered, washed with alcohol and dried in vacuo.

$$R_2SnCl_2 + K^+[C_{14}H_{10}N_6BO_4]^- \rightarrow [R_2Sn(C_{14}H_{10}N_6BO_4)Cl] + KCl$$

$$R_3SnCl + K^+[C_{14}H_{10}N_6BO_4]^- \rightarrow [R_3Sn(C_{14}H_{10}N_6BO_4)] + KCl$$

where R_2 = Dimethyl and dibutyl

R_3 = Trimethyl, tributyl and triphenyl

Hydrotris (5-nitroindazolyl) borate complexes

The stoichiometric amount of ice cold solution of hydrotris (5-nitroindazolyl) borate was poured into an alcoholic solution of dibutyltindichloride 1 g (3.29 mmol), dimethyltindichloride 1 g (4.52 mmol), tributyltinchloride 1 g (3.08 mmol), trimethyltinchloride 1 g (5.01 mmol) or triphenyltinchloride 1 g (2.59 mmol) and stirred for about six hours, keeping the temperature at $0^{o}C$. The KCl was filtered off and the solution was kept at $0^{o}C$ for about a week whereupon the yellowish crystals were obtained which were worked up as described earlier :

$$R_2SnCl_2 + K^{+}[C_{21}H_{13}N_9BO_6]^{-} \rightarrow [R_2Sn(C_{21}H_{13}N_9BO_6)Cl] + KCl$$

$$R_3SnCl + K[C_{21}H_{13}N_9BO_6]^{-} \rightarrow [R_3Sn(C_{21}H_{13}N_9BO_6)] + KCl$$

where R_2 = Dimethyl and dibutyl

R_3 = Trimethyl, tributyl and triphenyl

Tetrakis (5-nitroindazolyl) borate complexes

The complexation was carried out by treating an ice cold stoichiometric amount of the ligand, tetrakis (5-nitroindozolyl) borate with dibutyltindichloride 1 g (3.29

mmol) or dimethyltindichloride 1 g (4.55 mmol), tributyltinchloride 1 g (3.08 mmol), trimethyltinchloride 1 g (5.01 mmol) or triphenyltinchloride 1 g (2.59 mmol) dissolved in 25 ml of methanol and stirred for about eight hours. When the KCl was filtered off, the resulting solution was kept at $0^{o}C$ which yielded light yellowish solid after about 7 days after the following reaction :

$$R_2SnCl_2 + K^{+}[C_{28}H_{16}N_{12}BO_8]^{-} \rightarrow [R_2Sn(C_{28}H_{16}N_{12}BO_8)Cl] + KCl$$

and

$$R_3SnCl + K[C_{28}H_{16}N_{12}BO_8]^{-} \rightarrow [R_3Sn(C_{28}H_{16}N_{12}BO_8)] + KCl$$

where R_2 = Dimethyl and dibutyl

R_3 = Trimethyl, tributyl and triphenyl

Dihydrobis-, Hydrotris- and Tetrakis (6-nitroindazolyl) borate complexes

The complexes of dialkyltindihalides and trialkyltinhalide with potassium dihydrobis-, hydrotris-, and tetrakis (6-nitroindazolyl) borates were prepared using the same procedure.

Analysis and Physical Measurements

The complexes were analysed for metal content employing standard procedures [6,7]. The analysis of carbon,

hydrogen and nitrogen were done by the Departmental Micro-analytical laboratory. Infrared spectra were run on a Perkin-Elmer 621 spectrophotometer.

RESULTS AND DISCUSSION

The formation of these ligands and the stoichiometry of the complexes (1:1) have been established by the results of elemental analysis (Table 1). Some important i.r. frequencies of the ligands and their metal derivatives are tabulated (Table 2).

The i.r. spectra of these ligands do not show any band in the region 3500-3000 cm^{-1} which rules out the presence of N-H linkage [8]. The appearence of a band at around 1395 cm^{-1}, absent in free nitronidazole, indicates the formation of a new B-N bond [9]. This observation is indicative of the fact that all the N-H linkages have been replaced by B-N linkage [2,10]. Presence of a broad peak with slight splitting in the region 2460-2250 cm^{-1} in the i.r. spectra of the dihydrobis- salt indicate the presence of B-H bond [1,11]. The splitting indicates that the two hydrogens are not in the same plane [12,13] which is in agreement with the tetrahedral nature of BH_4^- ion [14,15]. In case of the hydrotris ligands, the i.r. spectra show only a single absorption peak

Table 1

Analytical Data of the ligands and their complexes

Complexes	MP (°C)	Yield (%)	Elemental Analysis % C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Sn Found (Calcd)	% Cl Found (Calcd)	Conductance $ohm^{-1}cm^2mol^{-1}$
$K^+[H_2B(5\text{-}NIz)_2]^-$	210	85	44.60 (44.68)	2.61 (2.65)	22.21 (22.34)	-	-	0.0027
$[H_2B(5\text{-}NIz)_2(Me_2SnCl)]$	>250	71	36.79 (36.88)	3.00 (3.07)	16.20 (16.13)	22.56 (22.67)	6.78 (6.82)	0.0042
$[H_2B(5\text{-}NIz)_2(Bu_2SnCl)]$	>225	69	43.54 (43.67)	4.66 (4.63)	13.79 (13.89)	19.47 (19.52)	5.80 (5.87)	0.0047
$[H_2B(5\text{-}NIz)_2(Me_3Sn)]$	>250	65	40.77 (40.80)	3.82 (3.80)	16.77 (16.80)	23.56 (23.60)	-	0.0048
$[H_2B(5\text{-}NIz)_2(Bu_2Sn)]$	>250	72	49.80 (49.84)	5.88 (5.91)	13.44 (13.41)	18.80 (18.84)	-	0.0037
$[H_2B(5\text{-}NIz)_2(Ph_3Sn)]$	>270	70	55.89 (55.97)	3.61 (3.64)	12.20 (12.24)	17.17 (17.20)	-	0.0031
$K^+[H_2B(6\text{-}NIz)_2]^-$	220	87	44.98 (44.70)	2.48 (2.68)	22.27 (22.36)	-	-	0.0029
$[H_2B(6\text{-}NIz)_2(Me_2SnCl)]$	>270	73	36.81 (36.92)	3.00 (3.12)	16.12 (16.20)	22.39 (22.76)	6.74 (6.90)	0.0049

Contd ...

Table 1 continued ...

Complexes	MP (°C)	Yield (%)	Elemental Analysis % C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Sn Found (Calcd)	% Cl Found (Calcd)	Conductance $ohm^{-1}cm^2mol^{-1}$
$[H_2B(6\text{-}NIz)_2(Bu_2SnCl)]$	>250	79	44.28 (43.67)	4.59 (4.68)	13.79 (13.91)	19.43 (19.56)	5.78 (5.93)	0.0044
$[H_2B(6\text{-}NIz)_2(Bu_2Me_3Sn)]$	>255	72	40.78 (40.86)	3.71 (3.80)	16.64 (16.80)	23.54 (23.60)	-	0.0059
$[H_2B(6\text{-}NIz)_2(Bu_3Sn)]$	>250	73	49.65 (49.84)	5.86 (5.91)	13.40 (13.41)	18.76 (18.84)	-	0.0050
$[H_2B(6\text{-}NIz)_2(Ph_3Sn)]$	>250	70	55.58 (55.61)	3.52 (3.66)	12.27 (12.30)	17.14 (17.26)	-	0.0064
$K^+[HB(5\text{-}NIz)_3]^-$	>250	82	46.78 (46.92)	2.37 (2.42)	23.39 (23.46)	-	-	0.0039
$[HB(5\text{-}NIz)_3(Me_2SnCl)]$	>250	73	40.32 (40.49)	2.63 (2.78)	18.41 (18.48)	17.27 (17.31)	5.13 (5.20)	0.0031
$[HB(5\text{-}NIz)_3(Bu_2SnCl)]$	>255	70	45.28 (45.40)	4.00 (4.04)	16.38 (16.45)	15.34 (15.41)	4.51 (4.63)	0.0038
$[HB(5\text{-}NIz)_3(Me\ Sn)]$	>255	75	43.57 (43.63)	3.10 (3.18)	19.00 (19.09)	17.72 (17.87)	-	0.0042

Contd ...

Table 1 continued ...

Complexes	MP (°C)	Yield (%)	Elemental Analysis % C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Sn Found (Calcd)	% Cl Found (Calcd)	Conductance $ohm^{-1}cm^2mol^{-1}$
$[HB(5\text{-}NIz)_3(Bu_3Sn)]$	>265	77	50.27 (50.31)	5.00 (5.08)	15.87 (16.01)	14.89 (14.99)	-	0.0047
$[HB(5\text{-}NIz)_3(Ph_3Sn)]$	>250	80	55.20 (55.25)	3.21 (3.30)	14.77 (14.87)	13.87 (13.93)	-	0.0044
$K^+[HB(6\text{-}NIz)_3]^-$	>250	82	46.98 (47.14)	2.40 (2.47)	23.40 (23.48)	-	-	0.0052
$[HB(6\text{-}NIz)_3(Me_2SnCl)]$	>250	75	40.44 (40.51)	2.72 (2.81)	18.46 (18.52)	17.27 (17.31)	5.21 (5.30)	0.0059
$[HB(6\text{-}NIz)_3(Bu_2SnCl)]$	>250	78	45.43 (45.51)	4.00 (4.11)	16.41 (16.48)	15.38 (15.47)	4.52 (4.60)	0.0048
$[HB(6\text{-}NIz)_3(Me_3Sn)]$	>255	73	43.57 (43.66)	3.00 (3.18)	18.97 (19.09)	17.70 (17.87)	-	0.0055
$[HB(6\text{-}NIz)_3(Bu_3Sn)]$	>250	65	50.18 (50.34)	5.00 (5.11)	15.90 (16.00)	14.87 (15.40)	-	0.0062
$[HB(6\text{-}NIz)_3(Ph_3Sn)]$	>260	70	55.24 (55.31)	3.27 (3.32)	14.83 (14.91)	13.90 (13.97)	-	0.0066

Contd...

Table 1 continued ...

Complexes	MP (°C)	Yield (%)	Elemental Analysis % C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Sn Found (Calcd)	% Cl Found (Calcd)	Conductance $ohm^{-1}cm^2mol^{-1}$
$K^+[B(5\text{-}NIz)_4]^-$	> 250	75	48.00 (48.13)	2.18 (2.29)	24.01 (24.06)	-	-	0.0048
$[B(5\text{-}NIz)_4(Me_2SnCl)]$	> 245	78	42.68 (42.72)	2.58 (2.61)	19.90 (19.94)	13.89 (13.00)	4.17 (4.21)	0.0044
$[B(5\text{-}NIz)_4(Bu_2SnCl)]$	> 250	74	46.55 (46.62)	2.97 (3.06)	18.07 (18.13)	12.69 (12.73)	3.77 (3.83)	0.0053
$[B(5\text{-}NIz)_4(Me_3Sn)]$	> 250	72	45.19 (45.25)	3.00 (3.04)	20.39 (20.43)	14.28 (14.35)	-	0.0051
$[B(5\text{-}NIz)_4(Bu_3Sn)]$	> 250	68	50.52 (50.63)	4.50 (4.53)	17.68 (17.72)	12.40 (12.44)	-	0.0039
$[B(5\text{-}NIz)_4(Ph_3Sn)]$	> 260	70	54.69 (54.76)	2.91 (3.07)	16.59 (16.66)	11.66 (11.70)	-	0.0037
$K^+[B(6\text{-}NIz)_4]^-$	> 250	80	48.00 (48.16)	2.22 (2.31)	23.89 (24.06)	-	-	0.0047
$[B(6\text{-}NIz)_4(Me_2SnCl)]$	> 255	60	42.69 (42.74)	2.60 (2.63)	19.89 (19.94)	13.80 (14.00)	4.10 (4.23)	0.0051

Contd...

Table 1 continued ...

Complexes	MP (°C)	Yield (%)	Elemental Analysis % C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Sn Found (Calcd)	% Cl Found (Calcd)	Conductance $ohm^{-1}cm^2mol^{-1}$
$[B(6\text{-}NIz)_4(Bu_2SnCl)]$	> 250	65	46.49 (46.55)	2.97 (3.06)	18.00 (18.13)	12.61 (12.73)	3.80 (3.83)	0.0048
$[B(6\text{-}NIz)_4(Me_3Sn)]$	> 255	65	46.09 (46.20)	2.91 (3.04)	20.37 (20.43)	14.27 (14.35)	-	0.0037
$[B(6\text{-}NIz)_4(Bu_3Sn)]$	> 260	66	50.55 (50.63)	4.48 (4.53)	17.70 (17.76)	12.40 (12.44)	-	0.0031
$[B(6\text{-}NIz)_4(Ph_3Sn)]$	> 275	71	54.61 (54.76)	3.00 (3.09)	16.51 (16.67)	11.59 (11.70)	-	0.0050

Table 2

Characteristic Infrared Bands (cm^{-1}) of the complexes

Complexes	B-H Stretching	B-N Stretching	C=N Stretching	NO_2 asymm. Stretching	Sn-N Stretching	Sn-Cl Stretching
$K^+[H_2B(5NIz)_2]^-$	2380(w) 2260(m)	1390(m)	1595(w)	1525(m)	-	-
$[H_2B(5\text{-}NIz)_2(Me_2SnCl)]$	2380(w) 2270(m)	1380(m)	1585(s)	1530(s)	340(m)	255(m)
$[H_2B(5\text{-}NIz)_2(Bu_2SnCl)]$	2360(m) 2260(s)	1390(w)	1570(m)	1535(m)	370(s)	230(s)
$[H_2B(5\text{-}NIz)_2(Me_3Sn)]$	2375(s) 2260(m)	1385(w)	1580(w)	1515(w)	335(s)	-
$[H_2B(5\text{-}NIz)_2(Bu_3Sn)]$	2370(m) 2260(m)	1400(m)	1565(w)	1525(w)	350(s)	-
$[H_2B(5\text{-}NIz)_2(Ph_3Sn)]$	2370(w) 2250(m)	1380(w)	1575(w)	1530(m)	360(m)	-
$K^+[H_2B(6\text{-}NIz)_2]^-$	2460(w) 2380(w)	1390(m)	1680(w)	1520(s)	-	-
$[H_2B(6\text{-}NIz)_2(Me_2SnCl)]$	2460(m) 2370(w)	1380(s)	1665(m)	1510(m)	355(m)	270(s)

Contd ...

Table 2 continued ...

Complexes	B-H Stretching	B-N Stretching	C=N Stretching	NO_2 asymm. Stretching	Sn-N Stretching	Sn-Cl Stretching
$[H_2B(6\text{-}NIz)_2(Bu_2SnCl)]$	2450(w) 2380(w)	1385(m)	1650(m)	1525(m)	380(s)	240(s)
$[H_2B(6\text{-}NIz)_2(Me_3Sn)]$	2450(s) 2370(w)	1380(m)	1670(w)	1520(s)	340(m)	-
$[H_2B(6\text{-}NIz)_2(Bu_3Sn)]$	2470(w) 2365(w)	1395(m)	1655(m)	1530(m)	335(s)	-
$[H_2B(6\text{-}NIz)_2(Ph_3Sn)]$	2465(m) 2370(m)	1380(w)	1660(w)	1525(m)	340(m)	-
$K^+[HB(5\text{-}NIz)_3]^-$	2380(w)	1395(w)	1575(s)	1520(m)	-	-
$[HB(5\text{-}NIz)_3(Me_2SnCl)]$	2390(w)	1390(w)	1545(s)	1535(m)	335(s)	245(m)
$[HB(5\text{-}NIz)_3(Bu_2SnCl)]$	2390(w)	1395(w)	1550(s)	1520(m)	355(m)	260(s)
$[HB(5\text{-}NIz)_3(Me_3Sn)]$	2400(m)	1390(w)	1550(s)	1525(m)	355(s)	-
$[HB(5\text{-}NIz)_3(Bu_3Sn)]$	2380(w)	1385(m)	1560(m)	1500(m)	345(m)	-
$[HB(5\text{-}NIz)_3(Ph_3Sn)]$	2385(w)	1380(w)	1540(s)	1530(m)	340(m)	-
$K^+[HB(6\text{-}NIz)_3]^-$	2400(w)	1380(m)	1670(w)	1520(s)	-	-

Contd...

Table 2 continued ...

Complexes	B-H Stretching	B-N Stretching	C=N Stretching	NO_2 asymm. Stretching	Sn-N Stretching	Sn-Cl Stretching
$[HB(6\text{-}NIz)_3(Me_2SnCl)]$	2400(w)	1370(m)	1655(s)	1520(m)	360(s)	230(s)
$[HB(6\text{-}NIz)_3(Bu_2SnCl)]$	2410(w)	1370(m)	1650(m)	1510(s)	365(m)	270(m)
$[HB(6\text{-}NIz)_3(Me_3Sn)]$	2420(m)	1375(s)	1640(s)	1525(m)	350(w)	-
$[HB(6\text{-}NIz)_3(Bu_3Sn)]$	2400(w)	1380(m)	1660(s)	1510(s)	345(m)	-
$[HB(6\text{-}NIz)_3(Ph_3Sn)]$	2410(w)	1380(w)	1650(m)	1530(m)	355(m)	-
$K^+[B(5\text{-}NIz)_4]^-$	-	1390(m)	1570(s)	1500(s)	-	-
$[B(5\text{-}NIz)_4(Me_2SnCl)]$	-	1390(w)	1555(s)	1500(m)	345(m)	260(m)
$[B(5\text{-}NIz)_4(Bu_2SnCl)]$	-	1380(m)	1540(s)	1515(m)	360(w)	235(m)
$[B(5\text{-}NIz)_4(Me_3Sn)]$	-	1400(m)	1540(s)	1510(m)	370(w)	-
$[B(5\text{-}NIz)_4(Bu_3Sn)]$	-	1385(w)	1560(m)	1500(w)	400(s)	-
$[B(5\text{-}NIz)_4(Ph_3Sn)]$	-	1380(w)	1545(s)	1500(m)	350(m)	-

Contd...

Table 2 continued ...

Complexes	B-H Stretching	B-N Stretching	C=N Stretching	NO_2 asymm. Stretching	Sn-N Stretching	Sn-Cl Stretching
$K^+[B(6\text{-}NIz)_4]^-$	-	1380(m)	1680(m)	1520(s)	-	-
$[B(6\text{-}NIz)_4(Me_2SnCl)]$	-	1390(w)	1635(m)	1520(s)	355(w)	250(m)
$[B(6\text{-}NIz)_4(Bu_2SnCl)]$	-	1380(w)	1620(w)	1510(m)	390(w)	245(s)
$[B(6\text{-}NIz)_4(Me_3Sn)]$	-	1385(w)	1660(s)	1510(m)	375(m)	-
$[B(6\text{-}NIz)_4(Bu_3Sn)]$	-	1380(m)	1640(s)	1500(m)	370(m)	-
$[B(6\text{-}NIz)_4(Ph_3Sn)]$	-	1380(w)	1650(s)	1520(m)	340(w)	-

m = medium, s = sharp, and w = weak

in 2460-2250 cm^{-1} region unlike the dihydrobis analogues which confirm the presence of a single B-H linkage in the molecules. The spectra of the tetrakis ligands do not exhibit any band in this region due to the absence of B-H bond because all the four hydrogen atoms of the borohydride moiety have been replaced by the B-N bond involving four nitroindazole molecule. The characteristic frequencies of nitroindazole molecule appear in the spectra of all these ligands at their appropriate positions and they all retain their shapes and intensities. The band in the region 1570-1595 cm^{-1} have been assigned to the C=N stretching frequency [16]. The symmetric and antisymmetric NO_2 stretching frequencies occur in the region 1520 cm^{-1} and 1352 cm^{-1} respectively [17] and a band at 1630 cm^{-1} has been assigned to the ring frequency. The probable structures of the dihydrobis-, hydrotris- and tetrakis ligands are shown in Figure 1-6.

All the complexes derived from these ligands show some common features. The nitroindazole molecule have got three potential coordination sites, viz, the pyrrolic nitrogen (=NH), the pyridyl nitrogen (≡N) and the nitro group ($-NO_2$). On the basis of i.r. studies on the complexes of nitroindazoles it has been found [17] that pyrrolic (=NH) nitrogen is more coordination active although coordination via the pyridyl (≡N) nitrogen has not been completely ruled

out. However, in none of the complexes the nitro group was suggested to take part in the coordination as the $-NO_2$ group stretching frequencies are only slightly shifted which is attributable to the inductive effect.

The complexes of dihydrobis (5-nitroindazolyl) borate and dihydrobis (6-nitroindazolyl) borate have been characterized after studying their i.r. spectra. A comparison of i.r. spectra of the ligands and those of the complexes suggest the involvement of only pyridyl nitrogen in coordination. This is inferred from the observed negative shift in the C=N stretching frequencies in the complexes. The B-N and NO_2 stretching frequencies have been found to apparently undergo no change after coordination indicating that neither the nitro group nor pyrrolic nitrogens are involved in the coordination.

In case of hydrotris (5-nitroindazolyl) borate and hydrotris (6-nitroindazolyl) borate complexes the bands in the high frequency region are not metal sensitive since they originate in the heterocyclic and aromatic ring of the ligands. However, some minor, but nevertheless important, shifts and changes have been observed for some bands after coordination which provides some clue to the probable coordination site. No changes have been observed in the stretching

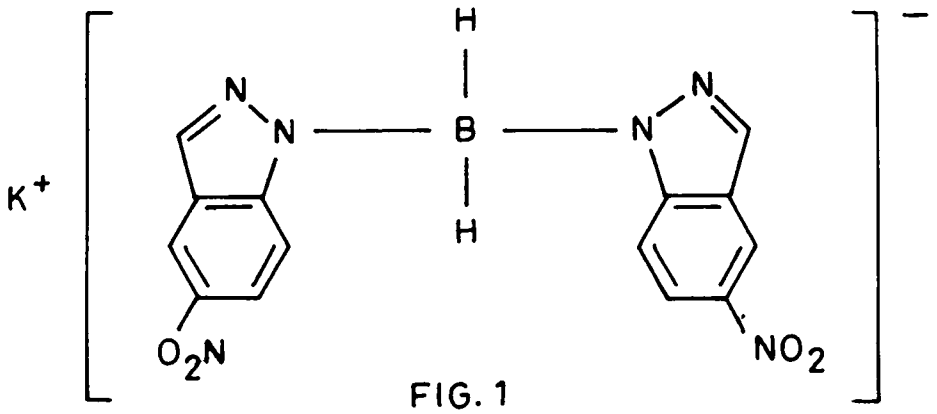


FIG. 1

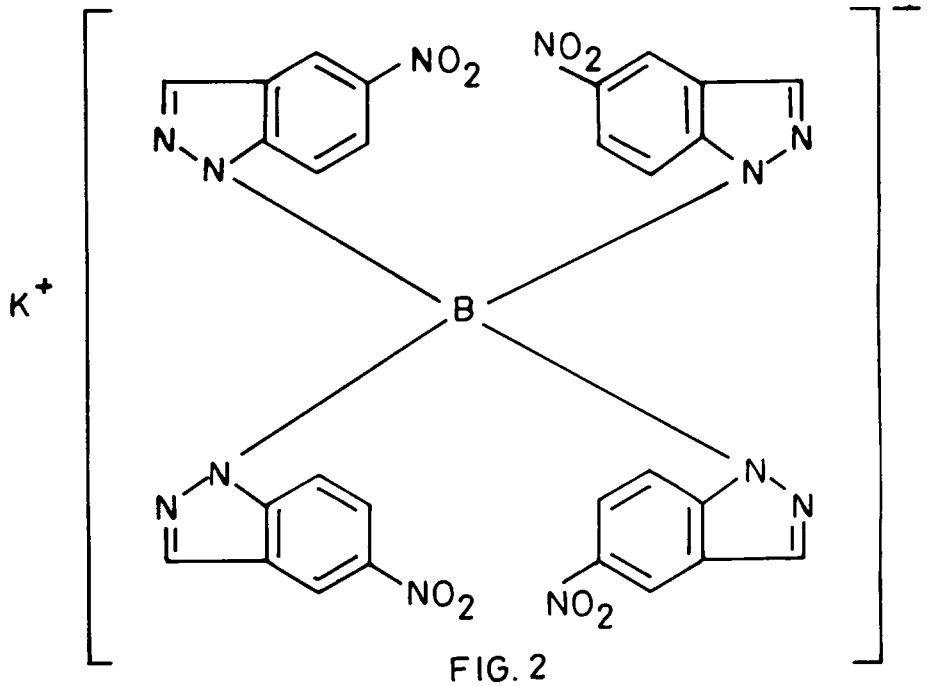


FIG. 2

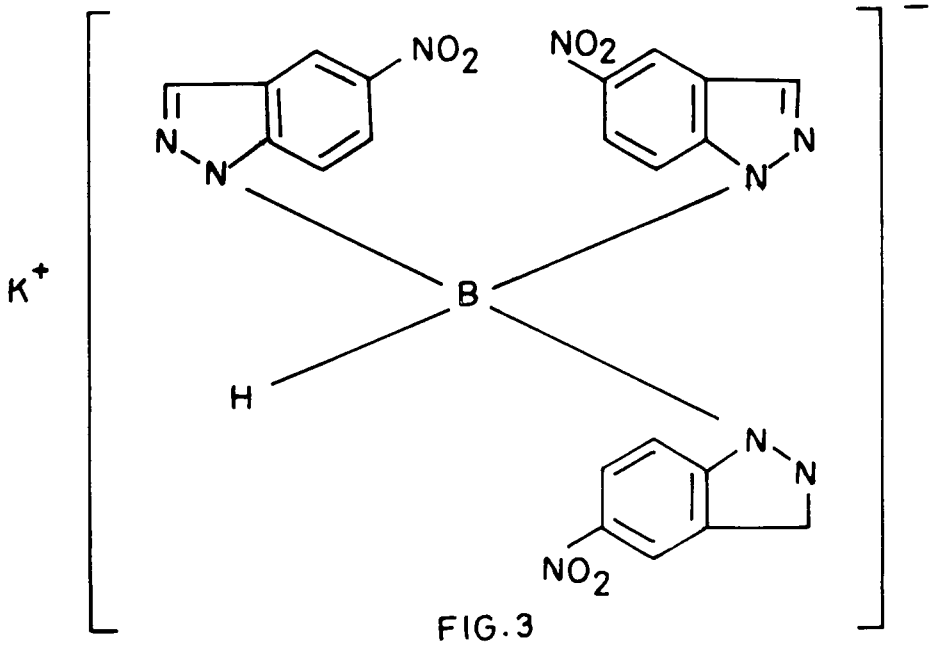


FIG. 3

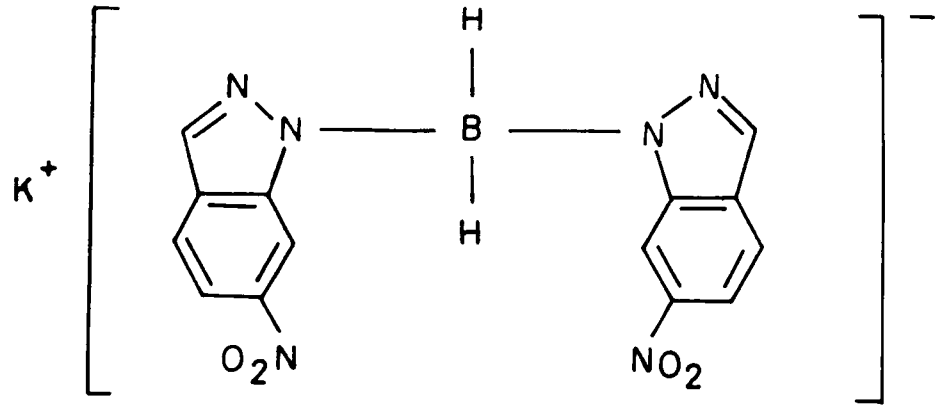


FIG. 4

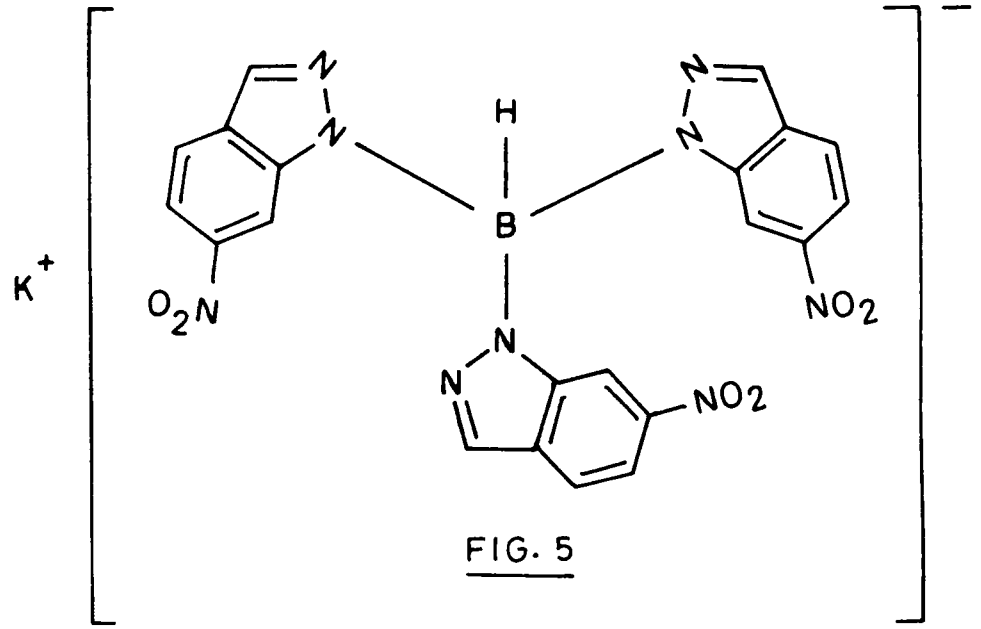


FIG. 5

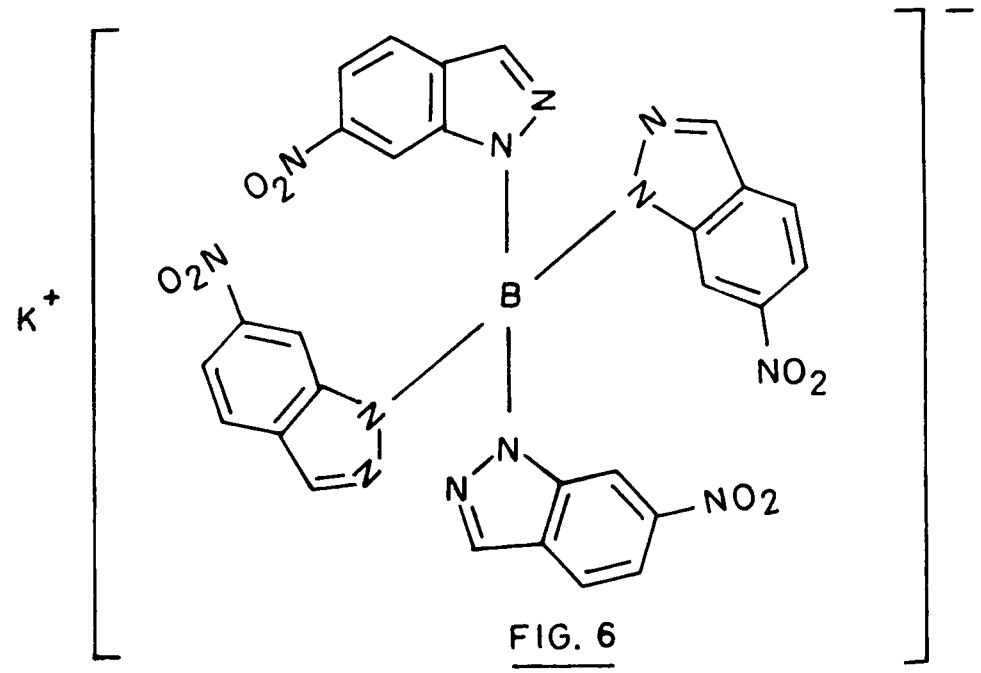
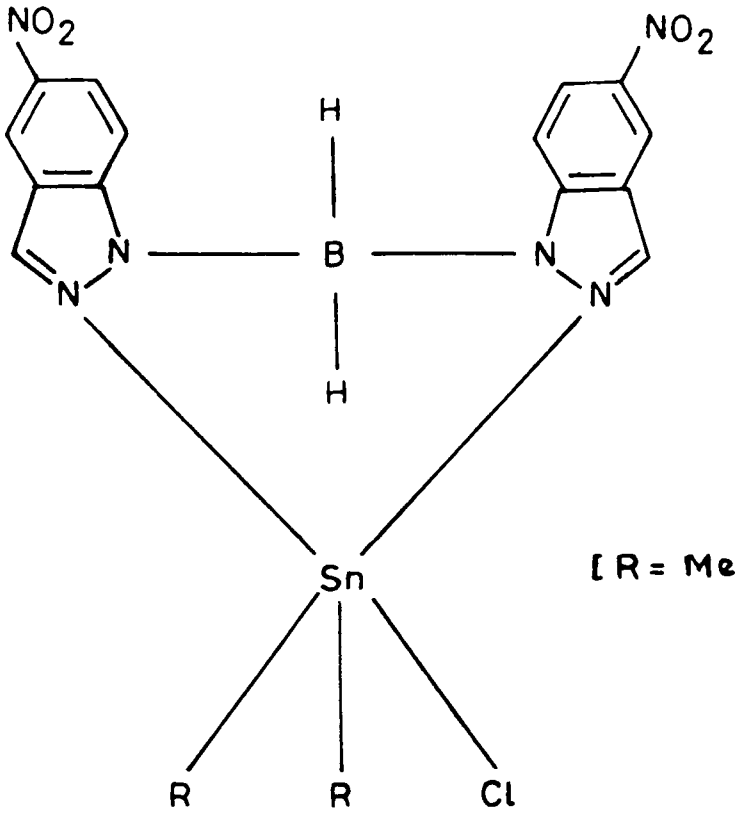


FIG. 6

frequencies of the NO_2 group and the B-H or B-N linkages indicating the non involvement of pyrrolic nitrogen atom or the NO_2 group. The observed negative shift of about 5-35 cm^{-1} upon complexation in the C=N stretching frequency suggest that only the pyridyl nitrogen atom takes part in coordination.

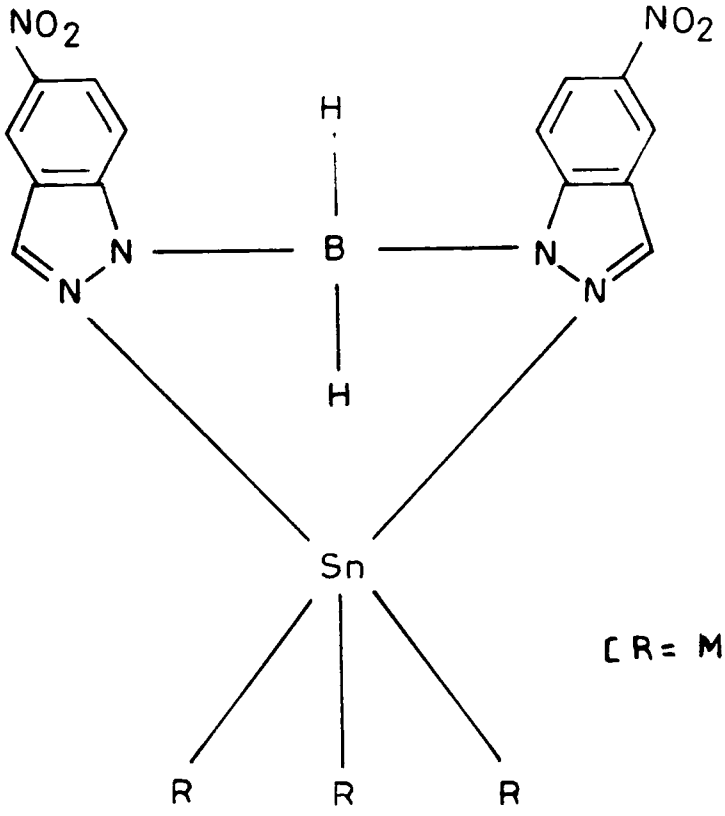
The i.r. spectra of tetrakis (5-nitroindazolyl) borate and tetrakis (6-nitroindazolyl) borate complexes show a shift to lower wave number in C=N stretching frequency. The other characteristic frequencies of the ligands are practically unaffected after coordination. These observations are indicative of coordination via only pyridyl nitrogen atom of the ligands and the other possible coordination sites such as the pyrrolic nitrogens and the nitro groups do not seem to be involved in coordination.

The spectra in the far i.r. region for all complexes show bands in the region 400-335 cm^{-1}, assigned, to Sn-N stretching vibrations but the assignment of these frequencies are rather uncertain as Sn-C stretching frequencies and some ligand frequencies also fall in the same region. The complexes of dialkyltindihalides show a single band in the region 230-270 cm^{-1} attributed to Sn-Cl stretching frequencies. These frequencies are found to be lowered by about 100 cm^{-1} compared with those of the parent compound due to an increase



[R = Me, Bu]

FIG. 7



[R = Me, Bu, Ph]

FIG. 8

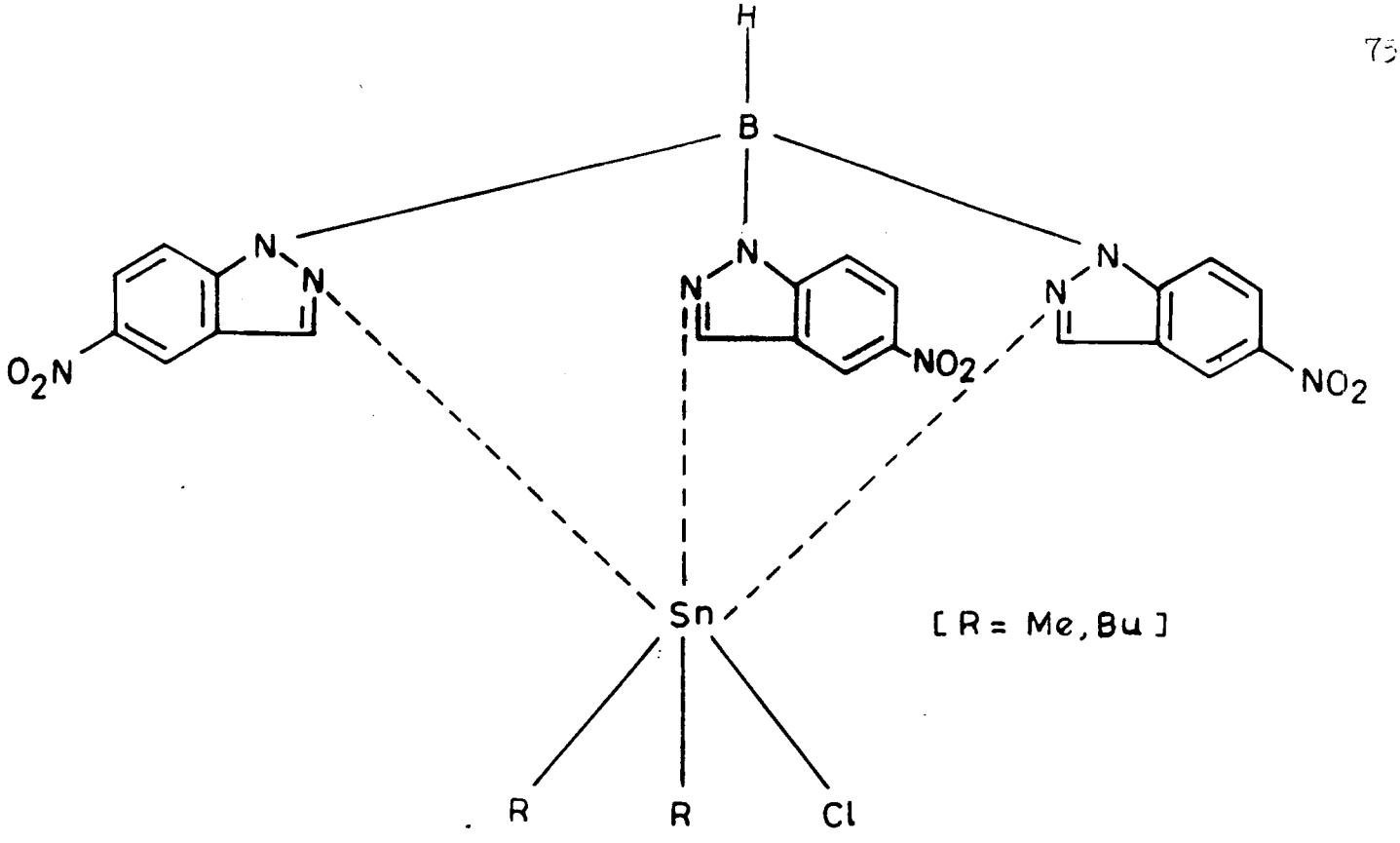

H
B
N
N
O_2N
N
N
NO_2
N
N
NO_2
Sn
R
R
Cl
[R = Me, Bu]

FIG. 9

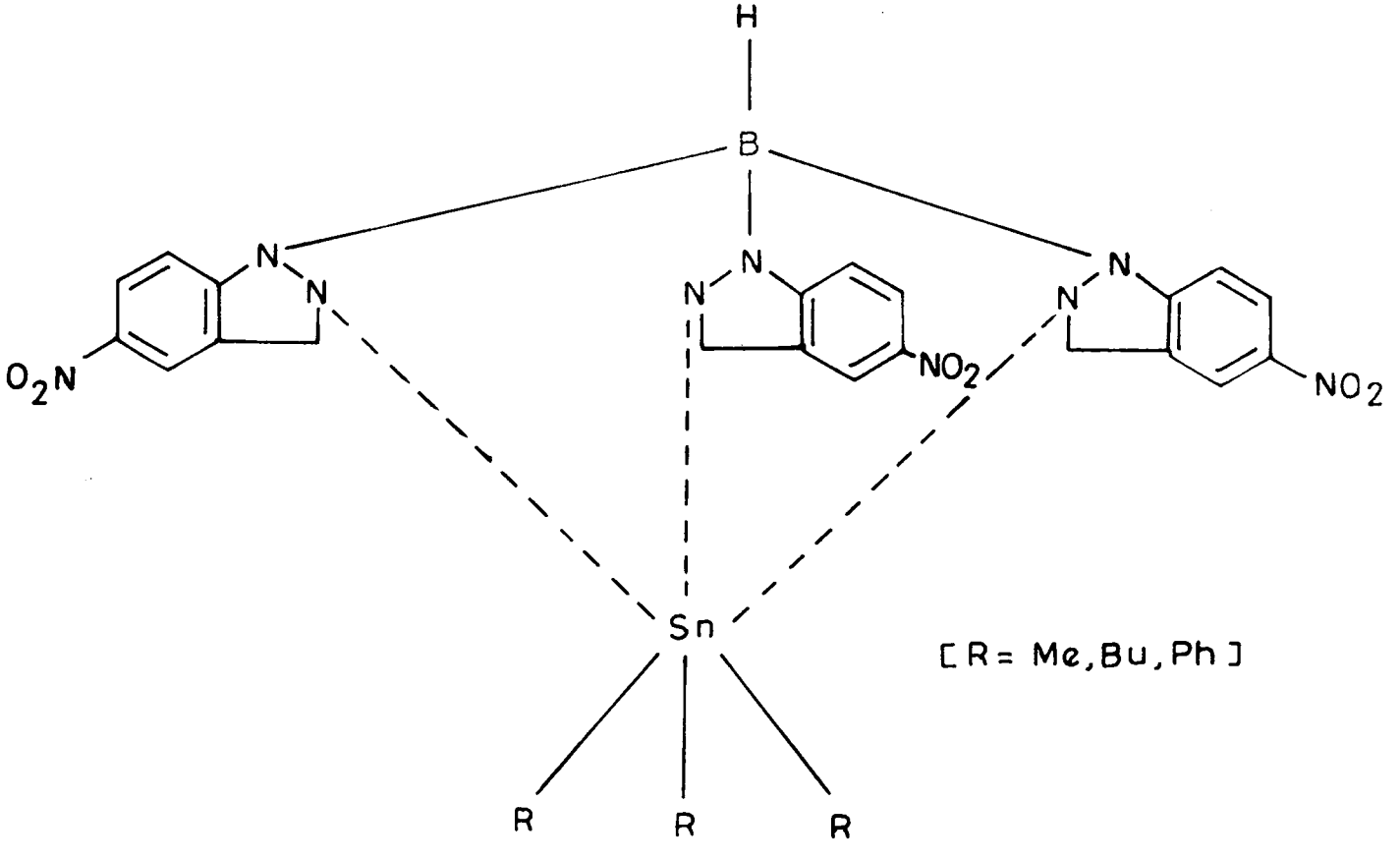
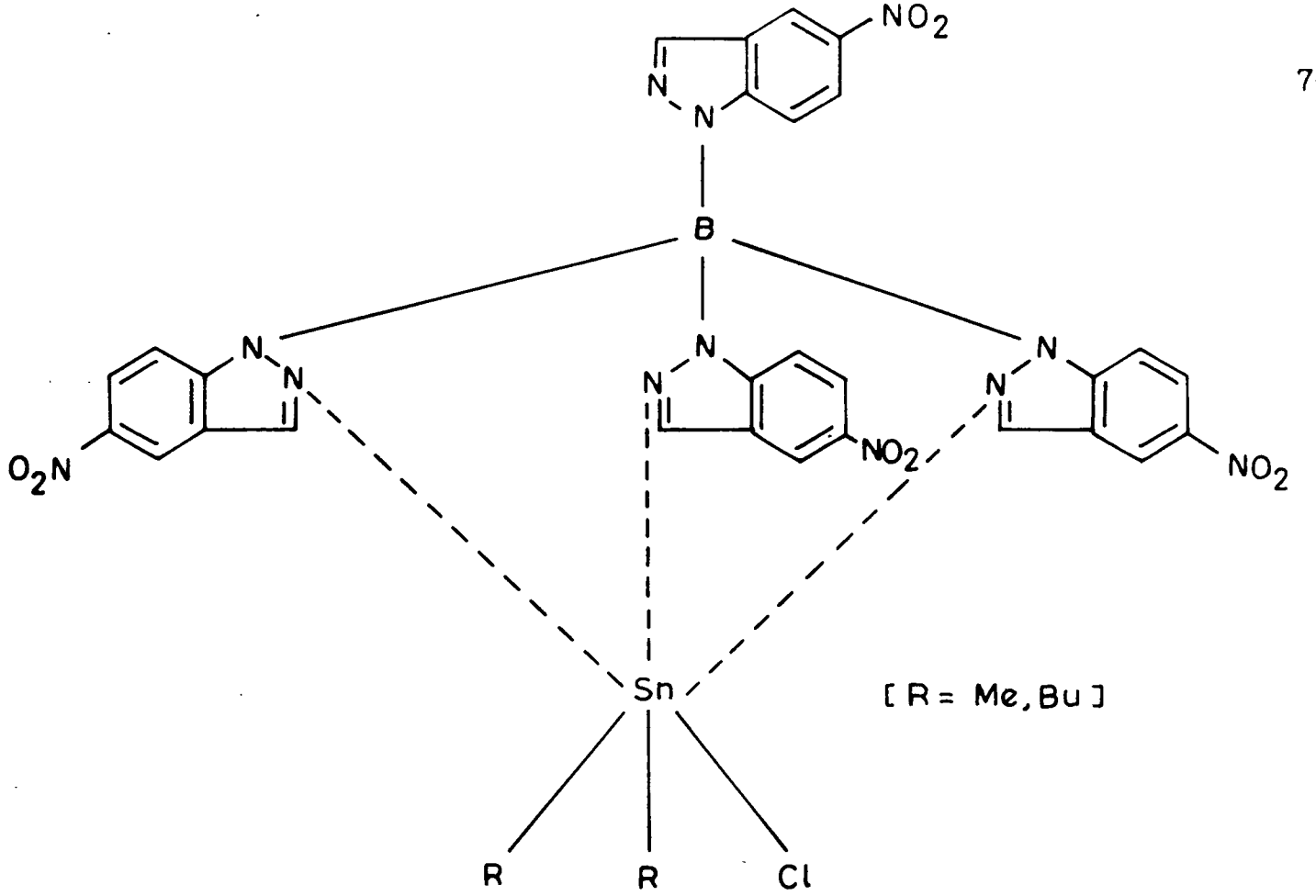
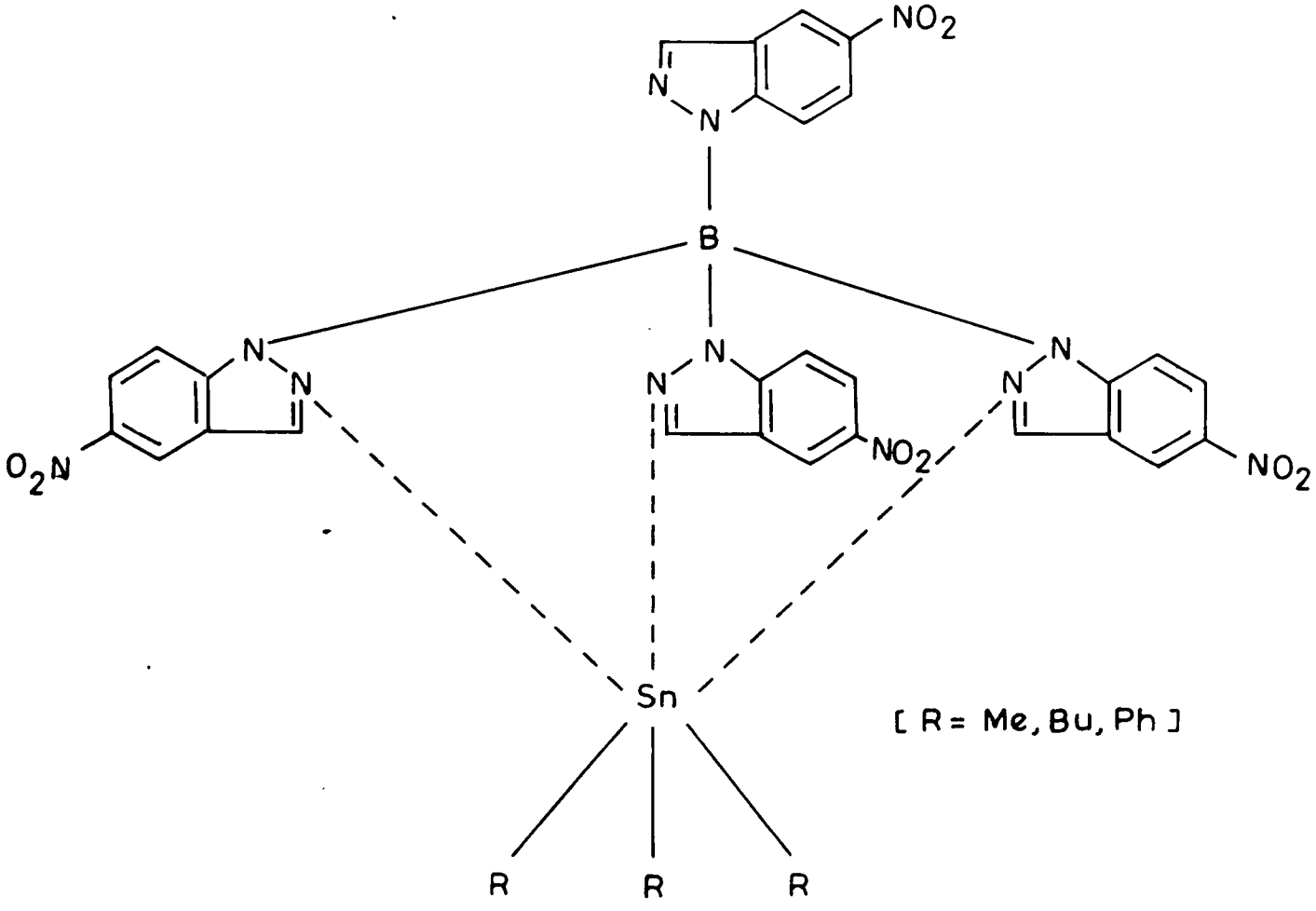

H
B
N
N
O_2N
N
N
NO_2
N
N
NO_2
Sn
R
R
R
[R = Me, Bu, Ph]

FIG. 10



[R = Me, Bu]

FIG. 11



[R = Me, Bu, Ph]

in the coordination number of the tin atom. The position of Sn-Me, Sn-Bu and Sn-Ph absorption bands remain unaltered after coordination when Sn atom undergoes a change in its coordination number [18,19].

In view of the above observations a square pyramidal geometry for the dihydrobis complexes and octahedral geometry for hydrotris- and tetrakis complexes have been proposed. In hydrotris and tetrakis complexes six coordinated tin is bonded to three alkyl groups and three indazolyl groups. The hexa-coordination around the tin atom in the tetrakis complexes could be achieved only when the ligand acts as a tridentate one. The proposed structure of the complexes have been shown in figures 7-12.

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C H A P T E R IV

COMPLEXES OF ORGANOTIN(IV) HALIDES WITH POLY(IMIDAZOLYL)BORATE ANIONS

CHAPTER IV

COMPLEXES OF ORGANOTIN (IV) HALIDES WITH POLY (IMIDAZOLYL) BORATE ANIONS

INTRODUCTION

The chemistry of metal complexes of imidazoles has received considerable attention in the last few years [1-5] mainly due to its applications in understanding some biological phenomena. Recently in our laboratory a series of anionic ligand of the type $[Hn\ B\ (Iz)_{4-n}]^-$ (where n = 2, 1 and 0 and Iz = imidazole residue) and several of their first row transition metal complexes [6,7] have been synthesized and characterized. A perusal of literature reveals that no work has been done so far on the complexes of these ligands with alkyltinhalides. It was, therefore, considered interesting to synthesize the complexes of various alkyltins with these ligands in order to probe the behaviour of these ligands towards the tin moiety and the properties of the new tin moiety thus formed.

EXPERIMENTAL

Imidazole (Sisco), dimethyltindichloride, dibutyltin dichloride, trimethyltinchloride, triphenyltinchloride (all Fluka), tributyltinchloride (E. Merck), and potassium boro-

hydride (BDH) were used as received.

Preparation of ligands

Potassium dihydrobis (imidazolyl) borate

For the synthesis of potassium dihydrobis (imidazolyl) borate a mixture of potassium borohydride 0.39 g (7.34 mmol) and imidazole 1 g (14.7 mmol) in a 1:2 molar ratio was ground to a fine powder and transferred into a round bottom flask and was refluxed with 30 ml of dry DMF for about twelve hours when 2 equivalent moles of hydrogen were evolved according to the following equation. The hydrogen was collected over water. The reaction mixture yielded a colourless solid after cooling to room temperature. The solid was washed and dried in vacuo.

$$KBH_4 + 2C_3H_4N_2 \rightarrow K^+[C_6H_8N_4B]^- + 2H_2$$

Potassium hydrotris (imidazolyl) borate

Potassium borohydride 0.27 g (4.90 mmol) and imidazole 1 g (14.7 mmol) were mixed together in 1:3 moler ratio and refluxed in 40 ml of dry DMF for about twenty four hours when 3 equivalent moles of hydrogen gas was evolved, after the following reaction. The colourless crystalline solid was obtained after cooling the mixture to 25°C.

$$KBH_4 + 3C_3H_4N_2 \rightarrow K^+[C_9H_{10}N_6B]^- + 3H_2$$

Potassium tetrakis (imidazolyl) borate

The above ligand was prepared by reacting potassium borohydride 0.19 g (3.51 mmol) and imidazole 1 g (14.7 mmol) in a 1:4 molar ratio under reflux in 50 ml of dry DMF for about thirty six hours when all the 4 equivalent moles of hydrogen gas was evolved. The resulting colourless solid was separated out, washed and dried under reduced pressure.

The reaction may be depicted as follows :

$$KBH_4 + 4C_3H_4N_2 \rightarrow K^+[C_{12}H_{12}N_8B]^- + 4H_2$$

Preparation of Complexes

All the complexes were prepared by taking the above prepared ligands and alkyltinhalides in a 1:1 ratio.

Dihydrobis (imidazolyl) borate complexes

The stoichiometric amount of $K^+[H_2B(Iz)_2]^-$ in 20 ml of methanol and dibutyltindichloride 1 g (3.29 mmol), dimethyltindichloride 1 g (4.52 mmol), tributyltinchloride 1 g (3.08 mmol), trimethyltinchloride 1 g (2.59 mmol) or triphenyltinchloride 1 g (2.59 mmol) each in 20 ml of methanol were mixed and stirred magnetically in a round bottom flask previously

cooled to 0°C. The precipitated KCl was filtered off and the reaction mixture was allowed to warm to room temperature with stirring for about 5-6 hours. On standing for about a week's time at 0°C the concentrated solution yielded white crystals.

$$R_2SnCl_2 + K^+[C_6H_8N_4B]^- \rightarrow [R_2Sn(C_6H_8N_4B)Cl] + KCl$$

$$R'_3SnCl + K^+[C_6H_8N_4B]^- \rightarrow [R_3Sn(C_6H_8N_4B)] + KCl$$

where R = Methyl or butyl

R′ = Methyl, butyl or phenyl

Hydrotris (imidazolyl) borate complexes

The complexation was carried out by pouring the stoichiometric amount of ice cold ligand solution in 20 ml of dry methanol into ice cold solution of dibutyltindichloride 1 g (3.29 mmol), dimethyltindichloride 1 g (4.52 mmol), tributyltinchloride 1 g (3.08 mmol), trimethyltinchloride 1 g (5.08 mmol) or triphenyltinchloride 1 g (2.59 mmol) respectively in 20 ml of methanol and stirred at room temperature for about 8 hours. When KCl was precipitated off, the mixture was kept at 0°C for about a week. The complexes separated out as white crystalline product.

$$R_2SnCl_2 + K^+[C_9H_{10}N_6B]^- \rightarrow [R_2Sn(C_9H_{10}N_6B)Cl] + KCl$$

$$R'_3SnCl + K^+[C_9H_{10}N_6B]^- \rightarrow [R_3Sn(C_9H_{10}N_6B)] + KCl$$

where R = Methyl or butyl

R′ = Methyl, butyl or phenyl

Tetrakis (imidazolyl) borate complexes

An ice cold solution of stiochiometric amount of the ligand, potassium tetrakis (imidazolyl) borate, in 20 ml of methanol was added into methanolic solution of dibutyltin-dichloride 1 g (3.29 mmol), dimethyltindichloride 1 g (4.55 mmol), tributyltinchloride 1 g (3.08 mmol), trimethyltin-chloride 1 g (5.01 mmol) or triphenyltinchloride 1 g (2.59 mmol) and stirred for about 10-12 hours. After the removal of the precipitated KCl, the resulting solution was kept at 0^oC for several days. The white crystalline solids were filtered, washed and dried in vacuo.

$$R_2SnCl_2 + K^+[C_{12}H_{12}N_8B]^- \rightarrow [R_2Sn(C_{12}H_{12}N_8B)Cl] + KCl$$

$$R'_3SnCl + K[C_{12}H_{12}N_8B] \rightarrow [R_3Sn(C_{12}H_{12}N_8B)] + KCl$$

where R = Methyl and butyl

R′ = Methyl, butyl and phenyl

Physical Measurements and Analysis

The complexes were analysed for tin contents adopting standard procedures [8,9]. Carbon, hydrogen and nitrogen analyses were done in microanalytical laboratory of the department. Infrared (4000 - 650 cm^{-1}) and far infrared (650 - 200 cm^{-1}) spectra in KBr and Nujol mull respectively were recorded with a Perkin-Elmer spectrophotometer model 621. The ^{1}H nmr spectra (in D_2O and $CDCl_3$) were recorded on a varian A 60 instrument.

RESULTS AND DISCUSSION

The formation of ligands potassium dihydrobis (imidazolyl) borate, potassium hydrotris (imidazolyl) borate and potassium tetrakis(imidazolyl)borate was ascertained by the evolution of the corresponding 2 moles of hydrogen for dihydrobis, 3 moles for hydrotris and 4 moles for tetrakis ligand respectively during the course of the reaction. The analytical data are in agreement with the proposed composition of these ligands. Further evidence regarding the formation of ligands have been indicated by the i.r. spectra of these compounds. The i.r. spectra of all these ligands do not show any bands in the region 3300-3450 cm^{-1} characteristic of N-H bond which further confirms that the amino hydrogen atom of the imidazole has been replaced. The appearance of a broad multiplet in the region 2300-2450 cm^{-1} in case of dihydrobis ligand indicates the presence of a B-H linkage [10-12]. However, only a singlet appeared in this region for the hydrotris ligand. The absence of this band in case of the tetrakis salt suggests the replacement of all the four hydrogen atoms of the potassium tetrahydroborate.

A strong peak due to B-N vibration [13] is found in the region 1380-1400 cm^{-1} which is absent in the free imidazole. The characteristic frequencies of imidazole ring system

[14] occurring at 1590-1670 cm^{-1} (R_1), 1520-1660 cm^{-1} (R_2), 1490-1520 cm^{-1} (R_3) and at 1310-1330 cm^{-1} (R_4) are also found in the spectra. The probable structures of these ligands are shown in figures 13-15.

The analytical data of complexes prepared are given in Table 3. The results of elemental analyses reveal a M:L ratio of 1:1. The molar conductance of 10^{-3} M solution of the complexes in nitrobenzene exhibits the non-ionic character of these complexes. The probable binding sites available to the metal have been located by comparison of the i.r. spectra of the ligands and their complexes (Table 4). The i.r. spectra of all the complexes show bands in 1350-1400 cm^{-1} indicating the presence of the B-N bond. The observed B-H doublet at 2300-2400 cm^{-1} for dihydrobis-, a B-H singlet at 2400-2440 cm^{-1} for hydrotris- and non-appearence of the B-H peak for the tetrakis-complexes show the presence respectively of two, one and no hydrogen atom(s) attached to boron.

The characteristic ring stretching frequencies of the ligands do not show any appreciable change upon complex formation [14]. Some of these bands have been found to be either shifted by about 10-50 cm^{-1} or remain unaltered on complexation. These small shifts are, however, found to be nearly independent of the metal ions. This observation is

Table 3

Microanalytical data of the complexes

Complexes	MP (°C)	Yield (%)	Elemental Analysis % C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Sn Found (Calcd)	% Cl Found (Calcd)	Conductance $ohm^{-1}cm^2 moles^{-1}$
$K^+[H_2B(I_z)_2]^-$	285	68	38.86 (38.73)	4.39 (4.33)	30.01 (30.11)	-	-	4.36
$[H_2B(I_z)_2(Me_2SnCl)]$	270	62	29.00 (29.04)	4.27 (4.23)	16.86 (16.94)	35.61 (35.70)	10.63 (10.74)	5.23
$[H_2B(I_z)_2(Bu_2SnCl)]$	280	60	40.40 (40.52)	6.32 (6.27)	13.89 (14.51)	28.31 (28.46)	8.41 (8.54)	4.60
$[H_2B(I_z)_2(Me_3Sn)]$	268	64	34.79 (34.83)	5.40 (5.48)	18.00 (18.06)	37.89 (38.06)	-	4.70
$[H_2B(I_z)_2(Bu_3Sn)]$	290	67	49.62 (49.54)	8.08 (8.02)	12.67 (12.84)	26.91 (27.06)	-	5.06
$[H_2B(I_z)_2(Ph_3Sn)]$	275	59	58.16 (58.06)	4.53 (4.64)	11.10 (11.29)	23.68 (23.79)	-	4.55
$K^+[HB(I_z)_3]^-$	>300	55	42.56 (42.87)	3.77 (3.99)	33.10 (33.33)	-	-	4.28
$[HB(I_z)_3(Me_2SnCl)]$	>300	50	33.36 (33.29)	4.11 (4.03)	21.01 (21.18)	29.61 (29.73)	8.86 (8.95)	5.13
$[HB(I_z)_3(Bu_2SnCl)]$	>300	52	42.46 (42.42)	5.71 (5.82)	17.29 (17.48)	24.50 (24.55)	7.41 (7.38)	4.75

Contd...

Table 3 continued ...

Complexes	MP (°C)	Yield (%)	Elemental Analysis					Conductance $ohm^{-1}cm^2$ $moles^{-1}$
			% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Sn Found (Calcd)	% Cl Found (Calcd)	
$[HB(I_z)_3(Me_3Sn)]$	>300	49	32.81 (32.94)	5.41 (5.49)	24.19 (24.27)	34.00 (34.10)	-	5.27
$[HB(I_z)_3(Bu_3Sn)]$	>300	44	50.10 (50.19)	7.30 (7.37)	16.61 (16.73)	23.56 (23.50)	-	5.48
$[HB(I_z)_3(Ph_3Sn)]$	>300	54	57.68 (57.65)	4.32 (4.44)	14.82 (14.94)	20.88 (20.99)	-	4.77
$K^+[B(I_z)_4]^-$	>360	50	45.63 (45.30)	3.92 (3.80)	35.00 (35.22)	-	-	4.00
$[B(I_z)_4(Me_2SnCl)]$	>360	48	36.41 (36.32)	3.78 (3.89)	24.10 (24.20)	25.44 (25.51)	7.59 (7.67)	5.23
$[B(I_z)_4(Bu_2SnCl)]$	>360	45	43.83 (43.91)	5.40 (5.48)	20.52 (20.49)	21.50 (21.59)	6.40 (6.49)	4.48
$[B(I_z)_4(Me_3Sn)]$	>360	52	40.78 (40.72)	4.61 (4.75)	25.38 (25.33)	26.60 (26.69)	-	4.56
$[B(I_z)_4(Bu_3Sn)]$	>360	55	50.76 (50.70)	6.30 (6.33)	19.66 (19.72)	20.62 (20.77)	-	5.34
$[B(I_z)_4(Ph_3Sn)]$	>360	46	57.44 (57.32)	4.11 (4.29)	17.74 (17.83)	18.63 (18.79)	-	5.15

Molar conductance of 10^{-3}M solution in nitrobenzene

Table 4

Characteristic Infrared Bands for the complexes

Complexes	B-H stretching (cm^{-1})	Ring stretching (cm^{-1})				B-N stretching (cm^{-1})	Sn-N stretching (cm^{-1})	Sn-Cl stretching (cm^{-1})
		R_1	R_2	R_3	R_4			
$K^+[H_2B(Iz)_2]^-$	2380m 2420m	1610 1625	1530	1495	1320s	1390m	-	-
$[H_2B(Iz)_2(Me_2SnCl)]$	2345m 2410m	1595m 1630s	1540w	1490m	1320m	1365s	380m	255m
$[H_2B(Iz)_2(Bu_2SnCl)]$	2300m 2410m	1610m 1605m	1530m	1500m	1310m	1370m	270s	255s
$[H_2B(Iz)_2(Me_3Sn)]$	2370s 2400m	1590s 1620m	1535w	1500s	1320m	1370m	415m	-
$[H_2B(Iz)_2(Bu_2Sn)]$	2340m 2390m	1610m 1625w	1530m	1500m	1325s	1350w	390s	-
$[H_2B(Iz)_2(Ph_3Sn)]$	2340s 2370w	1610w 1820m	1530m	1490m	1310m	1360m	370s	-
$K^+[HB(Iz)_3]^-$	2440s	1650m 1660m	1520m	1495s	1330m	1400m	-	-
$[HB(Iz)_3(Me_2SnCl)]$	2420m	1640m 1660s	1520w	1490m	1320s	1390w	410s	230s
$[HB(Iz)_3(Bu_2SnCl)]$	2400m	1650m 1665m	1510m	1485w	1330m	1375s	320m	265s

Contd...

Table 4 continued ...

Complexes	B-H stretching (cm^{-1})	Ring stretching (cm^{-1})				B-N stretching (cm^{-1})	Sn-N stretching (cm^{-1})	Sn-Cl stretching (cm^{-1})
		R_1	R_2	R_3	R_4			
$[HB(Iz)_3(Me_3Sn)]$	2400s	1650m 1640s	1510m	1440m	1324w	1380m	430s	-
$[HB(Iz)_3(Bu_3Sn)]$	2410m	1640m 1670m	1520m	1480m	1320m	1380s	400m	-
$[HB(Iz)_3(Ph_3Sn)]$	2420s	1650m 1670m	1520s	1490m	1320w	1370m	415s	-
$K^+[B(Iz)_4]^-$	-	1650m 1620m	1530m	1495m	1330m	1400m	-	-
$[B(Iz)_4(Me_2SnCl)]$	-	1640s 1610m	1530s	1490m	1320m	1370m	395s	240m
$[B(Iz)_4(Bu_2SnCl)]$	-	1650w 1615m	1525m	1480w	1335s	1360m	335s	260m
$[B(Iz)_4(Me_3Sn)]$	-	1650m 1610m	1520s	1500m	1330m	1390w	435m	-
$[B(Iz)_4(Bu_3Sn)]$	-	1640m 1615s	1535w	1495m	1330m	1400s	400m	-
$[B(Iz)_4(Ph_3Sn)]$	-	1645m 1610m	1540s	1500w	1320m	1365m	420s	-

m = medium, s = sharp, w = weak

in agreement with earlier reports on the metal complexes of imidazole [14,15], It is, therefore, proposed that the pyridyl nitrogen atom has participated in bonding to the metal ion. The BH_2 peaks in the dihydrobis and B-H peaks in hydrotris complexes are shifted to lower frequency from their position in the free ligands. The B-N stretching bands in the tin derivatives of the ligands appears at slightly lower frequencies corresponding to the B-N vibrations in the free ligands.

The bands observed in the far i.r. spectra in the region 435-300 cm^{-1} are assigned to Sn-N stretching vibrations. However, because of the fact that the ligands and Sn-C stretching frequencies fall in the same region, the assignment of Sn-N stretching frequencies are rather ambiguous. The Sn-Cl stretching frequencies in case of dialkyltindihalide complexes occur in the range of 230-270 cm^{-1} which are found to be lowered by some 100 cm^{-1} compared with those of the parent compounds, due to an increase in the coordination number of the tin atom. These assignments are in excellent agreement with the values reported for a number of dialkyltin chelates [9-11].

^{1}H NMR spectra

The proton nmr spectrum of the ligand potassium

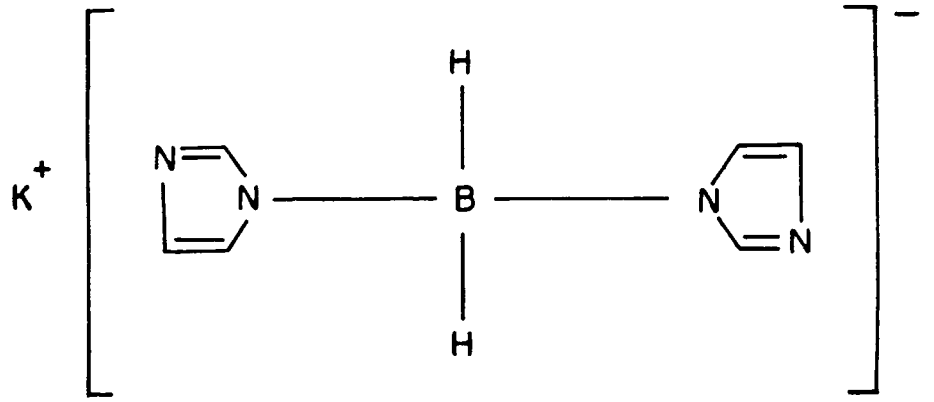


FIG. 13

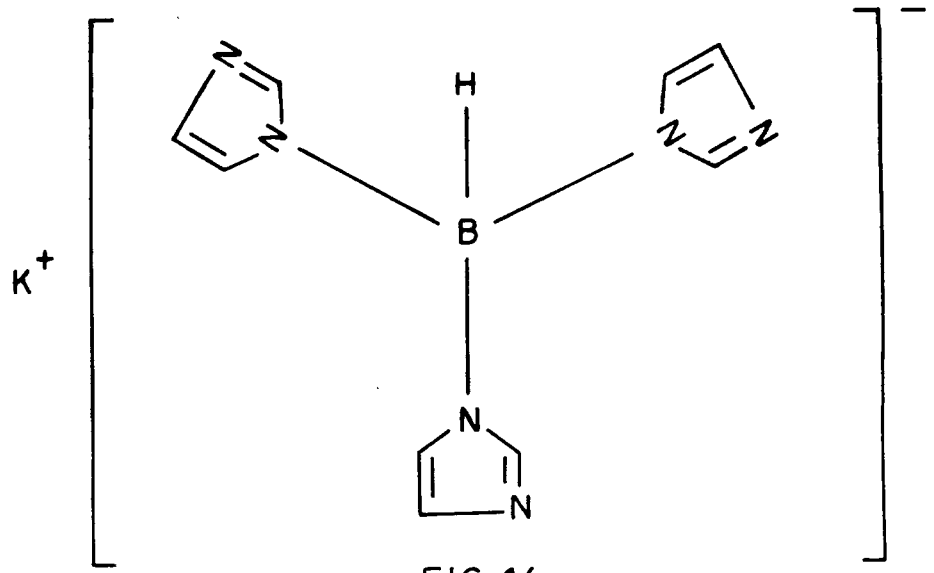


FIG. 14

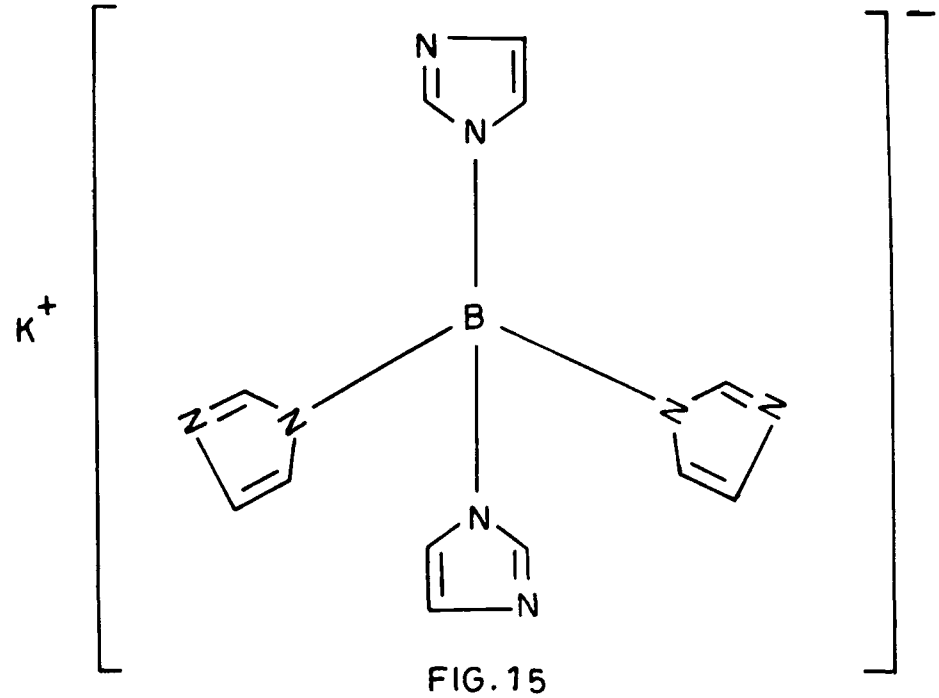
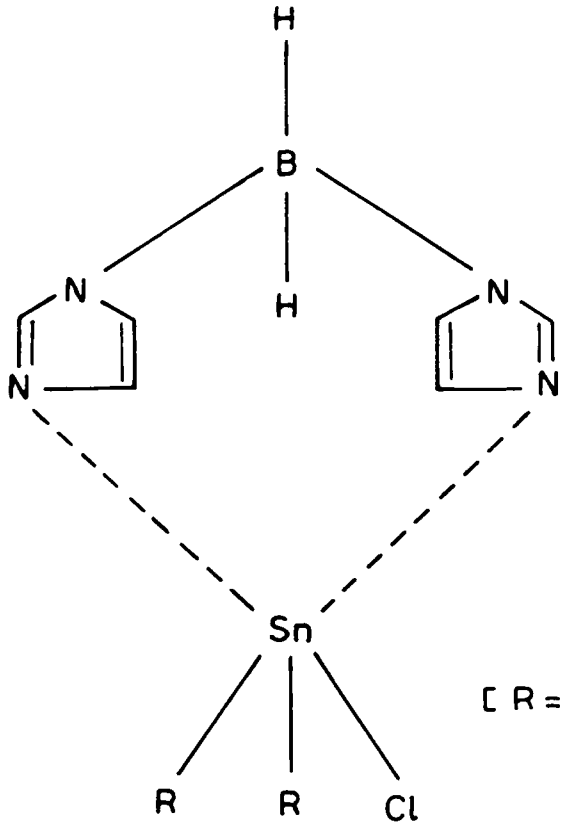


FIG. 15

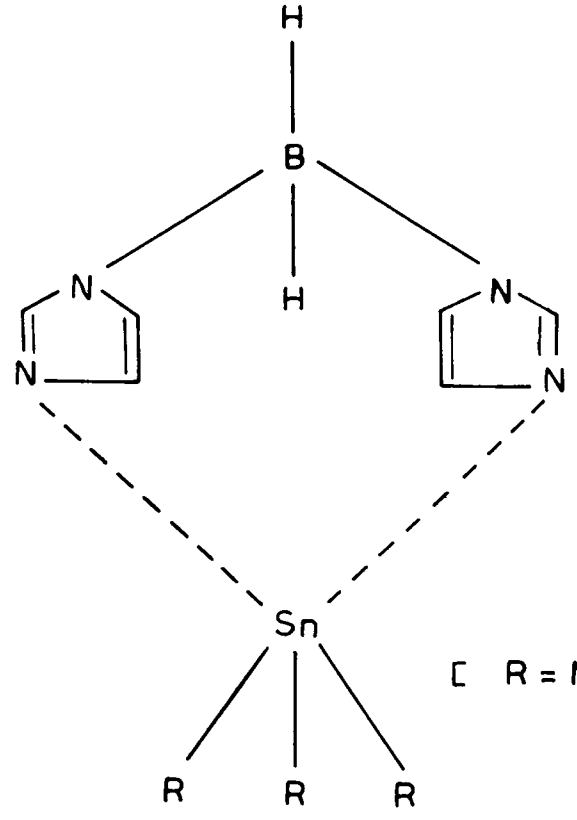
dihydrobis (imidazolyl) borate in D_2O exhibits a doublet at δ 7.19 and δ 7.09 and a triplet at δ 7.6 ppm in 1:1:1 ratio assigned to the C-H proton peaks of the imidazole nucleus. Due to the formation of the B-N bond the centre of equivalence of H-4 and H-5 protons in imidazole is lost and a doublet appears. The H-2 proton signal is also shifted from the free ligand value. The doublet observed for $B-H_2$ peak at δ 4.4 ppm is not very well resolved. For the hydrotris ligand, the three signals arising from C-H hydrogen are observed as doublet at δ 7.10 and δ 6.69 and a triplet at δ 7.56 ppm in a ratio 3:3:1. The B-H proton peak was feebly observed as a broad singlet at δ 4.7 ppm. The broadening may presumably be due to the interaction of the resonance with ^{11}B quaderpole (I = 3/2). In case of tetrakis ligands, the nmr spectrum reveals three peaks, as doublet at δ 7.28 and δ 6.86 and a not very well resolved triplet at δ 7.84 ppm in a 1:1:1 ratio.

The ^1H nmr of the dihydrobis- complexes in $CDCl_3$ show imidazolyl groups to be equivalent indicating their coordination to the tin moiety. On complexation the electron withdrawal by the tin group results in a marked shift to about δ 7.85 ppm from δ 7.19 ppm observed in the ligand in the proton peak adjacent to pyridyl nitrogen atom. The corresponding peak in the hydrotris- complexes are also shifted from δ 7.10 ppm to δ 7.82 ppm upon complex formation. Other



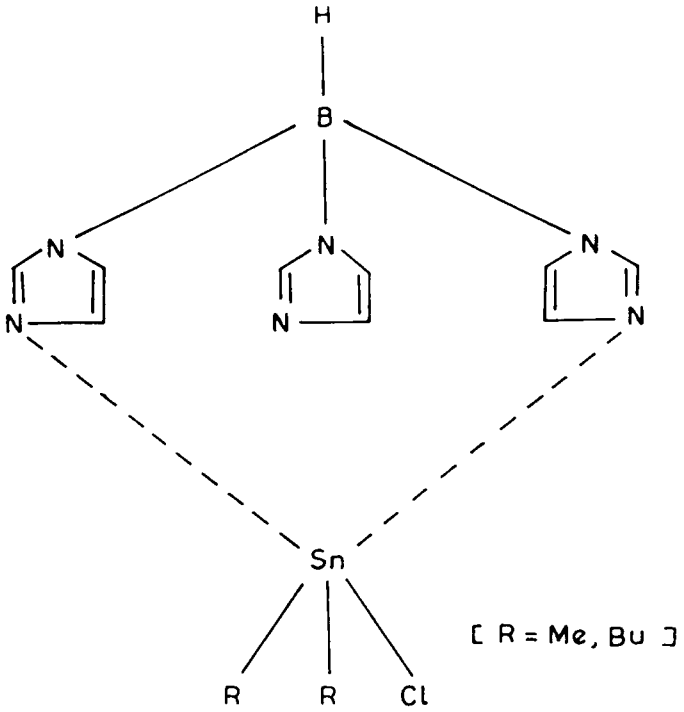
[R = Me, Bu]

FIG. 16



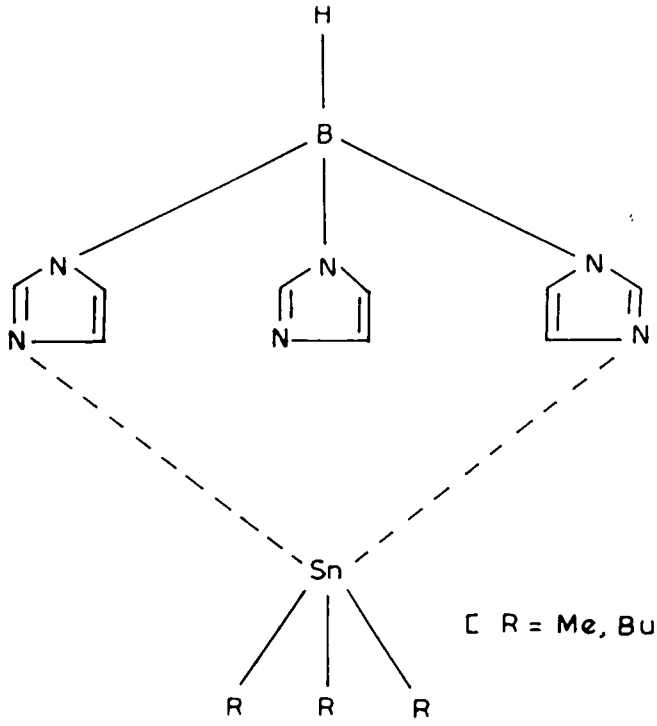
[R = Me, Bu, Ph]

FIG. 17



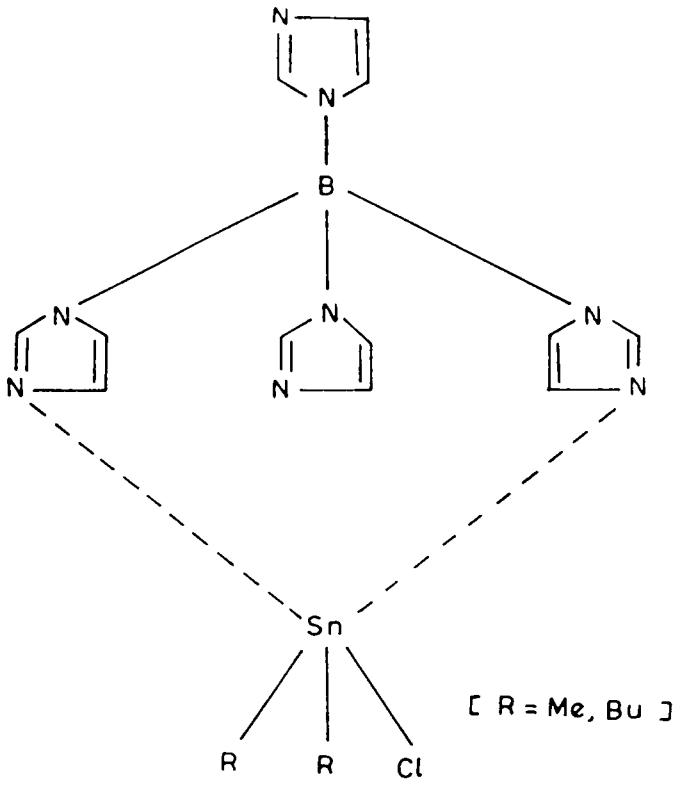
[R = Me, Bu]

FIG. 18



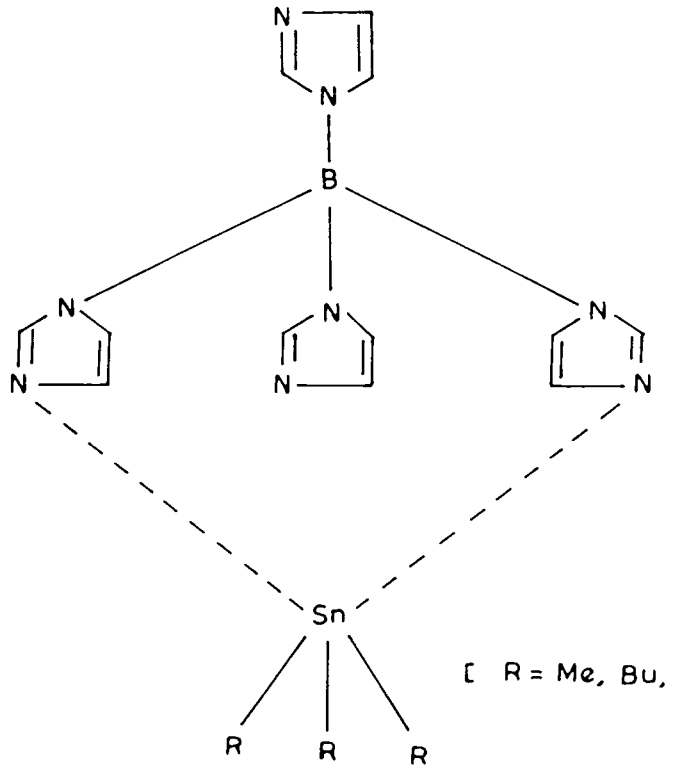
[R = Me, Bu, Ph]

FIG. 19



[R = Me, Bu]

FIG. 20



[R = Me, Bu, Ph]

FIG. 21

proton peaks appear at around δ 7.30, δ 6.70 (H-5) and δ 7.69, δ 7.75 (H-2) respectively, in the dihydrobis- and hydrotris- complexes. In case of tetrakis- complexes, tne spectra are consistent with the presence of two imidazole ring. The spectra consist of a doublet at about δ 7.28, δ 7.69, δ 6.89 ppm and a triplet at around δ 7.86 and δ δ 8.19 ppm. Three of these resonance peaks at around δ 7.67 (H-4), δ 7.29 (H-5) and δ 8.19 (H-2) have twice the intensity of the other indicating assignments as hydrogen atom of the three imidazolyl nuclei bound to tin atom.

The tin butyl, tin-methyl and tin-phenyl signals appear between δ 0.75-2.1, δ 0.50-0.8 and δ 8.1-8.3 ppm respectively in the corresponding complexes.

Thus a square pyramidal geometry for the dihydrobis complexes and octahedral geometry for the hydrotris and tetrakis complexes could be achieved only when the ligands acts as a tridentate one. The dihydrobis- and hydrotris complexes have five and six coordination for the tin atom involving two and three coordinated imidazole rings respectively. The tetrakis complexes are also hexacoordinated involving three coordinated imidazole rings and one uncoordinated ring. The proposed structures of the complexes are given in figures16-21.

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C H A P T E R V

SYNTHESIS AND STRUCTURAL STUDIES OF SOME PENTA- AND HEXACOORDINATED ORGANOTIN(IV) HALIDE COMPLEXES OF POLY (2-METHYLIMIDAZOLYL) BORATES

CHAPTER V

SYNTHESIS AND STRUCTURAL STUDIES OF SOME PENTA- AND HEXA-COORDINATED ORGANOTIN (IV) HALIDE COMPLEXES OF POLY (2-METHYLIMIDAZOLYL) BORATES.

INTRODUCTION

The coordination chemistry of several penta- and hexacoordinated organotin (IV) halide complexes of poly (imidazolyl) borate anions has been extensively reviewed in the previous chapter. As a further extention of our work in the area of boron-imidazole chemistry, it seemed desirable to synthesize the alkyltinhalide complexes of poly (2-methylimidazolyl) borate anions, which are still unknown in the chemical literature. The work in the present chapter is concerned with the synthesis and characterization of several alkyltinhalide complexes with above mentioned ligands in order to see whether the methyl substituted ligand behaves similarly to unsubstituted ligand.

EXPERIMENTAL

2-Methylimidazole (Sisco), metal chlorides (Fluka and E. Merck) and potassium tetrahydroborate (BDH) were obtained commercially. Dimethyl formamide and methanol (BDH) were used after purification.

Preparation of potassium dihydrobis (2-methylimidazolyl) borate

Potassium borohydride 0.32 g (6.08 mmol) and 2-methylimidazole 1 g (12.17 mmol) were mixed together and dissolved in ~25 ml of dry DMF. The contents were heated under reflux till the calculated amount of hydrogen gas was evolved. The solution after cooling, yielded a colourless solid which was filtered, washed repeatedly and dried in vacuo.

$$KBH_4 + 2C_4H_6N_2 \rightarrow K^+[C_8H_{12}N_4B]^- + 2H_2$$

Preparation of potassium hydrotris (2-methylimidazolyl) borate

A mixture of potassium tetrahydroborate 0.21 g (4.06 mmol) and 2-methylimidazole 1 g (12.17 mmol) were refluxed in ~40 ml of dry DMF until the theoretical amount (3 moles) of hydrogen was evolved. A colourless solid was obtained after cooling the mixture at room temperature.

$$KBH_4 + 3C_4H_6N_2 \rightarrow K^+[C_{12}H_{16}N_6B]^- + 3H_2$$

Preparation of potassium tetrakis (2-methylimidazolyl) borate

This ligand was prepared by mixing together potassium borohydride 0.16 g (3.04 mmol) and 2-methylimidazole 1 g (12.17 mmol) and refluxing the mixture with ~50 ml of dry DMF until all four moles of hydrogen gas were evolved. After cooling the solution at room temperature, a colourless solid was obtained which was filtered, washed and dried in vacuo.

$$KBH_4 + 4C_4H_6N_2 \rightarrow K^+[C_{16}H_{20}N_8B]^- + 4H_2$$

Preparation of the complexes

The complexes were synthesized by taking alkyltin-halides and the above prepared ligands in a 1:1 ratio.

Dihydrobis (2-methylimidazolyl)borate complexes

Complexation was carried out by taking stoichiometric amount of an ice cold solution of potassium dihydrobis (2-methylimidazolyl) borate in 25 ml of dry methanol and pouring it into ice cold solution of dibutyltindichloride 1 g (3.29 mmol), dimethyltindichloride 1 g (4.55 mmol), tributytinchloride 1 g (3.08 mmol), trimethyltinchloride 1 g (5.01 mmol) or triphenyltinchloride 1 g (2.59 mmol) in ~25 ml of

methanol and stirring magnetically for 5-6 hours. After removal of KCl, the solution was kept at 0°C for about a week. The white complexes were separated out which were filtered, washed and dried. The reaction may be represented as follows :

$$R_2SnCl_2 + K^+[C_8H_{12}N_4B]^- \rightarrow [R_2Sn(C_8H_{12}N_4B)Cl] + KCl$$

$$R_3SnCl + K^+[C_8H_{12}N_4B]^- \rightarrow [R_3Sn(C_8H_{12}N_4B)] + KCl$$

where R_2 = Dimethyl or dibutyl

R_3 = Trimethyl, tributyl or triphenyl

Hydrotris (2-methylimidazolyl)borate complexes

The stoichiometric amount of the ligand in ice cold state in 20 ml of dry methanol and dibutyltindichloride 1 g (3.29 mmol), dimethyltindichloride 1 g (4.55 mmol), tributyltinchloride 1 g (3.08 mmol), trimethyltinchloride 1 g (5.01 mmol) or triphenyltinchloride 1 g (2.59 mmol) were mixed and stirred at room temperature for about 6-7 hours. The precipitated KCl was filtered off and the reaction mixture was allowed to cool at 0°C for a week. White crystals were separated out which were filtered, washed and dried.

The reactions may be represented as follows :

$$R_2SnCl_2 + K^+[C_{12}H_{16}N_6B]^- \rightarrow [R_2Sn(C_{12}H_{16}N_6B)Cl] + KCl$$

$$R_3SnCl + K^+[C_{12}H_{16}N_6B]^- \rightarrow [R_3Sn(C_{12}H_{16}N_6B)] + KCl$$

where R_2 = Dimethyl or dibutyl

R_3 = Trimethyl, tributyl or triphenyl

Tetrakis (2-methylimidazolyl) borate complexes

The complexation was carried by taking stoichiometric amount of ice cold ligand potassium tetrakis (2-methyl imidazolyl) borate dissolved in 20 ml of dry methanol and mixing with dibutyltindichloride 1 g (3.29 mmol), dimethyltindichloride 1 g (4.55 mmol), tributyltinchloride 1 g (3.08 mmol), trimethyltinchloride 1 g (5.01 mmol) or triphenyltinchloride 1 g (2.59 mmol) each in 20 ml of methanol. The contents were stirred for about 10 hours. The precipitated KCl was filtered off and the remaining solution was kept at 0°C. After about a week, white crystalline product was obtained from the solution which was filtered, washed and dried in vacuo.

The reaction may be represented as follows :

$$R_2SnCl_2 + K^+[C_{16}H_{12}N_8B]^- \rightarrow [R_2Sn(C_{16}H_{12}N_8B)Cl] + KCl$$

$$R_3SnCl + K^+[C_{16}H_{12}N_8B]^- \rightarrow [R_3Sn(C_{16}H_{12}N_8B)] + KCl$$

where R_2 = Dimethyl or dibutyl

R_3 = Trimethyl, tributyl or triphenyl

Analysis and Physical Measurements

Metals were determined by standard procedures. Carbon hydrogen and nitrogen were estimated by microanalytical division at University Science College, Calcutta.

Infrared and far infrared spectra in KBr and Nujol mull respectively were recorded on a Perkin-Elmer 621 spectrophotometer and ^1H nmr spectra (in D_2O and $CDCl_3$) were recorded with a Varian A60 instrument.

RESULTS AND DISCUSSION

The formation of the ligand viz. potassium dihydrobis (2-methylimidazolyl) borate, potassium hydrotris (2-methylimidazolyl) borate and potassium tetrakis (2-methylimidazolyl) borate were established by ascertaining the evolution of the corresponding 2,3 or 4 equivalent moles of hydrogen gas respectively during the reactions. The ligands and their complexes were characterized by their elemental analysis, i.r. and n.m.r. spectral studies.

The results of elemental analysis are consistent with

the proposed composition of the ligands. The infrared spectrum does not contain any band that could be assigned as νN-H [1] in all the three ligands, but a doublet in case of dihydrobis- and a singlet in case of hydrotris- ligands appears in the region 2400-2480 cm^{-1} indicating the presence of B-H linkage. The splitting of the B-H frequency in case of dihydrobis ligand shows that the two hydrogen atoms on the boron do not lie in the same plane, which is in agreement with the tetrahedral nature of BH_4^- ion. No such band was observed in case of tetrakis- ligand. A strong band in the region 1370-1410 cm^{-1} indicates the presence of B-N stretching vibrations [2] which are absent in 2-methylimidazole. The spectrum also shows ring stretching bands, R_1, R_2, R_3 and R_4, of imidazole ring system [3]. The infrared spectra also contain absorption bands between 2840-2970, 1350-1365 and 1245-1255 cm^{-1} assigned to νCH_3, δ sym. CH_3 and $\nu C-CH_3$ modes respectively [4]. (figures22-24).

The elemental analysis data (Table 5) indicate that the complexes are formed in a 1:1 ratio. A low molar conductivity of these complexes in 10^{-3} M solution in nitrobenzene, suggests their non-ionic nature.

The bonding sites in the complexes have been located by the comparison of infrared spectra of the complexes and

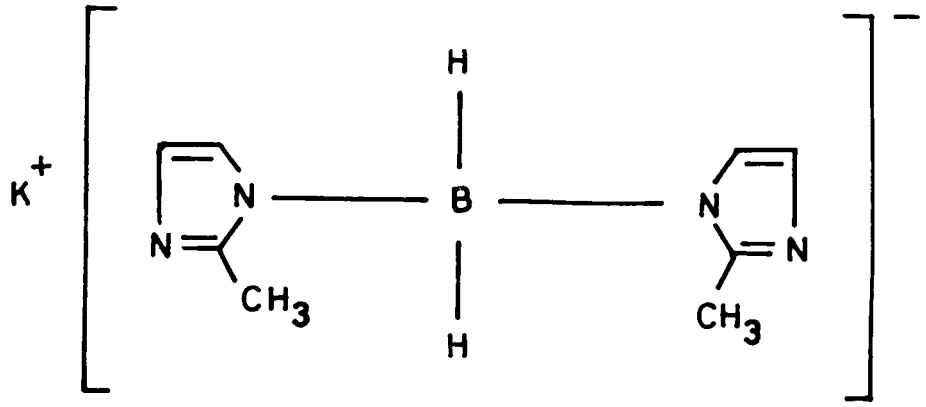


FIG. 22

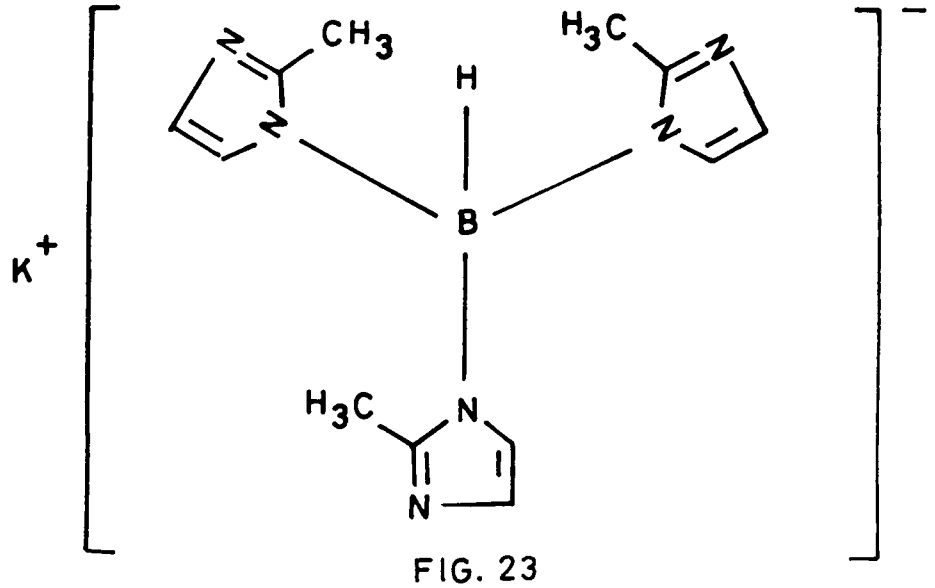


FIG. 23

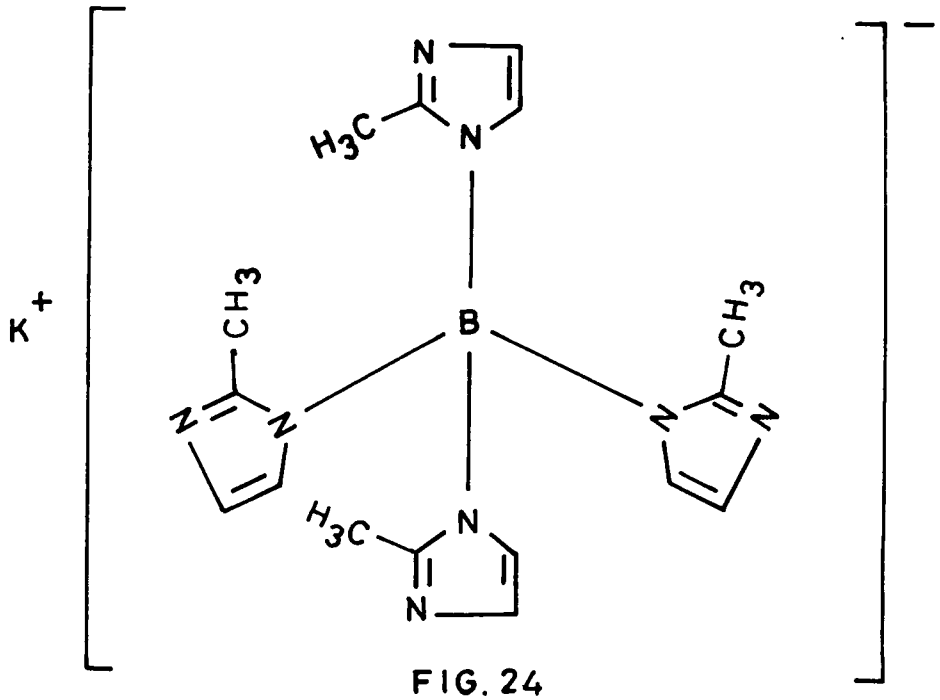


FIG. 24

the ligands (Table 6). The spectra of free ligands show recognisable bands in the region 1630-1320 cm^{-1} which may be assigned as ring stretching vibrations of imidazole ring system. On complexation, the position of these bands remain almost unaltered and the shifts in some of these vibrations have been found to be metal independent as in the case of some metal complexes of imidazole [3,5] where the coordination occurs via the pyridine-nitrogen. It is, therefore, proposed that the pyridyl nitrogen behaves as nitrogen donor atom. There is no marked shift in any of the B-H and B-N vibrations indicating the non-involvement of pyrrolic nitrogen in coordination.

The far infrared spectrum of the complexes consists of bands in the region 520-290 cm^{-1} assigned to Sn-N stretching vibrations, however the positions of these bands could not be confirmed as these stretching vibrations overlap with some of the ligands vibrations as well as Sn-C stretching frequencies in this region. Bands in the region 255-220 cm^{-1} are attributed to Sn-Cl stretching vibrations in the dialkyltin complexes. Evidently there is a marked decrease in the Sn-Cl stretching vibrations [6-8] with increasing coordination number of tin atom, an effect that agrees with a mainly ionic character of the Sn-Cl bond [9]. The tin-phenyl, tin-methyl and tin-butyl frequencies remain unchanged after coordination in all the complexes. This observation suggests that Sn-C

Table 5

Analytical data of the Complexes

Complexes	MP (°C)	Yield (%)	Elemental Analysis					Conductance $ohm^{-1}cm^2$ $moles^{-1}$
			% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Sn Found (Calcd)	% Cl Found (Calcd)	
$[H_2B(2\text{-}MeI_z)_2SnMe_2Cl]$	>300	55	33.13 (33.47)	4.97 (5.02)	15.70 (15.62)	32.76 (32.91)	9.98 (9.90)	5.01
$[H_2B(2\text{-}MeI_z)_2SnBu_2Cl]$	>300	60	42.97 (43.38)	6.86 (6.77)	12.38 (12.65)	26.58 (26.66)	8.00 (8.02)	4.60
$[H_2B(2\text{-}MeI_z)_2SnMe_3]$	>300	50	40.01 (39.05)	6.17 (6.21)	16.44 (16.56)	34.77 (34.91)	-	5.31
$[H_2B(2\text{-}MeI_z)_2SnBu_3]$	>300	60	51.66 (51.72)	8.38 (8.40)	12.00 (12.06)	25.40 (25.43)	-	5.26
$[H_2B(2\text{-}MeI_z)_2SnPh_3]$	>300	55	59.48 (59.54)	5.10 (5.15)	10.60 (10.68)	25.56 (25.51)	-	4.78
$[HB(2\text{-}MeI_z)_3SnMe_2Cl]$	>300	66	38.21 (38.31)	5.10 (5.01)	19.11 (19.15)	26.83 (26.90)	8.12 (8.09)	4.86
$[HB(2\text{-}MeI_z)_3SnBu_2Cl]$	>300	60	45.90 (45.93)	6.55 (6.50)	16.00 (16.07)	22.53 (22.58)	6.76 (6.79)	5.38
$[HB(2\text{-}MeI_z)_3SnMe_3]$	>300	55	43.00 (43.06)	5.93 (5.98)	20.13 (20.09)	28.17 (28.22)	-	5.26

Contd...

Table 5 continued ...

Complexes	MP (°C)	Yield (%)	Elemental Analysis % C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% Sn Found (Calcd)	% Cl Found (Calcd)	Conductance $ohm^{-1}cm^2$ $moles^{-1}$
$[HB(2\text{-}MeIz)_3SnBu_3]$	>300	48	53.04 (52.94)	7.79 (7.90)	15.36 (15.44)	21.61 (21.69)	-	4.40
$[HB(2\text{-}MeIz)_3SnPh_3]$	>300	54	59.63 (59.60)	5.11 (5.13)	13.86 (13.90)	15.59 (19.53)	-	4.80
$[B(2\text{-}MeIz)_4SnMe_2Cl]$	>300	50	41.61 (41.63)	5.00 (5.01)	21.54 (21.60)	22.84 (22.75)	6.44 (6.46)	5.31
$[B(2\text{-}MeIz)_4SnBu_2Cl]$	>300	53	47.73 (47.80)	6.36 (6.30)	18.61 (18.58)	19.56 (19.58)	5.80 (5.89)	5.26
$[B(2\text{-}MeIz)_4SnMe_3]$	>300	48	45.72 (45.78)	5.80 (5.82)	22.40 (22.48)	23.73 (23.69)	-	4.60
$[B(2\text{-}MeIz)_4SnBu_3]$	>300	40	53.80 (53.84)	7.56 (7.53)	17.88 (17.94)	18.86 (18.91)	-	4.75
$[B(2\text{-}MeIz)_4SnPh_3]$	>300	50	59.66 (59.64)	5.13 (5.11)	16.29 (16.37)	17.27 (17.25)	-	5.18

Table 6

Characteristic infrared bands for the complexes

Complexes	B-H Stretching (cm^{-1})	B-N Stretching (cm^{-1})	CH_3 Stretching (cm^{-1})	Ring Stretching (cm^{-1})				Sn-N Stretching (cm^{-1})	Sn-Cl Stretching (cm^{-1})
				R_1	R_2	R_3	R_4		
$[H_2B(2\text{-}MeI_z)_2SnMe_2Cl]$	2350m 2420m	1395s	2860s 2950s	1600s 1620s	1520m	1490m	1340m	460m	245s
$[H_2B(2\text{-}MeI_z)_2SnBu_2Cl]$	2340m 2410m	1380s	2840s 2950s	1610s 1620s	1530m	1500m	1340m	370s	245m
$[H_2B(2\text{-}MeI_z)_2SnMe_3]$	2360m 2410m	1380s	2850s 2950s	1580m 1610m	1530m	1510m	1340m	390m	-
$[H_2B(2\text{-}MeI_z)_2SnBu_3]$	2350m 2410m	1390s	2860s 2950s	1600s 1610s	1540m	1490m	1340m	450m	-
$[H_2B(2\text{-}MeI_z)_2SnPh_3]$	2370m 2410m	1380s	2860s 2950s	1590s 1610s	1530m	1500m	1340m	410m	-
$[HB(2\text{-}MeI_z)_3SnMe_2Cl]$	2400s	1410s	2960m 2850m	1620m 1610m	1545s	1480m	1325m	480m	250m
$[HB(2\text{-}MeI_z)_3SnBu_2Cl]$	2360s	1390s	2950m 2840m	1630m 1610m	1540m	1470m	1320m	520m	220m
$[HB(2\text{-}MeI_z)_3SnMe_3]$	2370m	1380m	2970m 2850m	1630m 1610m	1535m	1480m	1330m	470m	-

Contd...

Table 6 continued ...

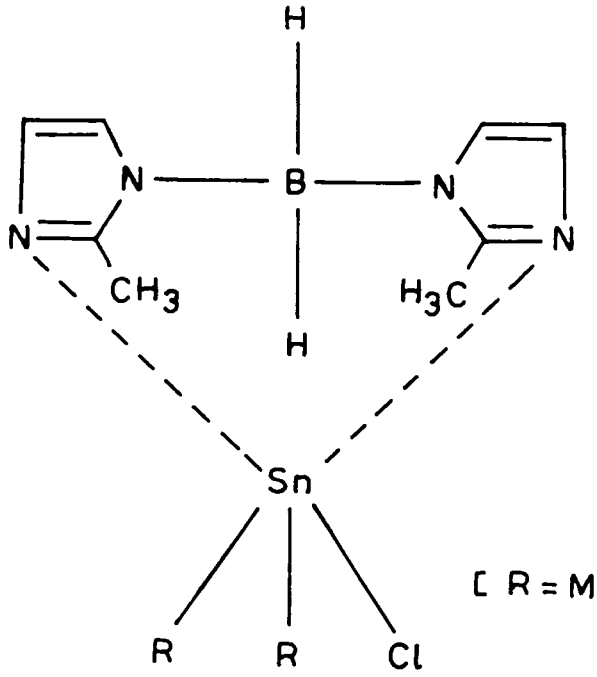
Complexes	B-H Stretching (cm^{-1})	B-N Stretching (cm^{-1})	CH_3 Stretching (cm^{-1})	Ring Stretching (cm^{-1})				Sn-N Stretching (cm^{-1})	Sn-Cl Stretching (cm^{-1})
				R_1	R_2	R_3	R_4		
$[HB(2\text{-}MeI_z)_3SnBu_3]$	2390s	1390s	2960m 2840m	1620m 1600m	1530m	1485m	1325m	300s	-
$[HB(2\text{-}MeI_z)_3SnPh_3]$	2410m	1400m	2960m 2860m	1610m 1600m	1545m	1480m	1320m	360m	-
$[B(2\text{-}MeI_z)_4SnMe_2Cl]$	-	1390m	2950m 2830m	1630m 1610m	1530m	1470m	1330m	410m	230m
$[B(2\text{-}MeI_z)_4SnBu_2Cl]$	-	1400m	2960m 2840m	1610m 1590m	1510m	1480m	1325m	330m	255m
$[B(2\text{-}MeI_z)_4SnMe_3]$	-	1395m	2950m 2840m	1620m 1605m	1520m	1485m	1320m	310m	-
$[B(2\text{-}MeI_z)_4SnBu_3]$	-	1390m	2940m 2830m	1610m 1580m	1525m	1475m	1330m	290m	-
$[B(2\text{-}MeI_z)_4SnPh_3]$	-	1385m	2950m 2820m	1630m 1595m	1525m	1485m	1330m	300m	-

bands in these compounds are relatively unaffected by changes in the coordination number of the central tin atom. Similar effect has been noted in various alkyl halide complexes with other ligands [7,10].

^{1}H nmr

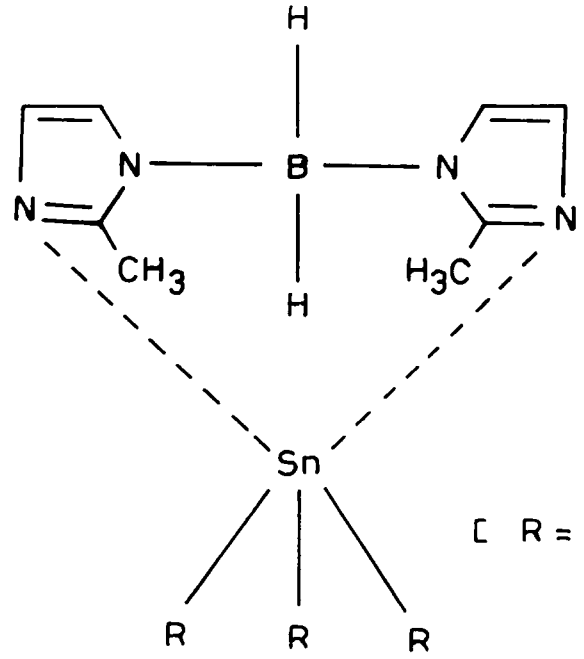
The proton magnetic resonance spectrum of the dihydrobis (2-methylimidazolyl) borate has been recorded in D_2O. The signals at δ 7.80 and δ 6.69 ppm are due to H-4 and H-5 protons of the imidazole nucleus. An ill resolved B-H_2 doublet is observed at about the same position (δ 4.6 ppm) as in the unsubstituted ligand [11]. For hydrotris- and tetrakis- ligands, these signals appear at δ 7.76 and δ6.67 ppm and δ 7.78 and δ 6.71 ppm respectively. The B-H peak is observed as a broad singlet at about δ 4.8 ppm. The broadening of this peak may be due to the interaction of resonance with ^{11}B quadrupole (I = 3/2). Further the ligands also show a singlet at δ 2.5 - δ 2.91 ppm for the methyl proton.

The proton peaks adjacent to the pyridyl nitrogen atom (H-4) of the ligands shift downfield in the spectra of the tin complexes (δ 7.95 ppm) indicating their deshielding. This is probably due to the donation of the lone pair of electrons by the nitrogen to the central tin atom due to the formation of a coordinate bond.



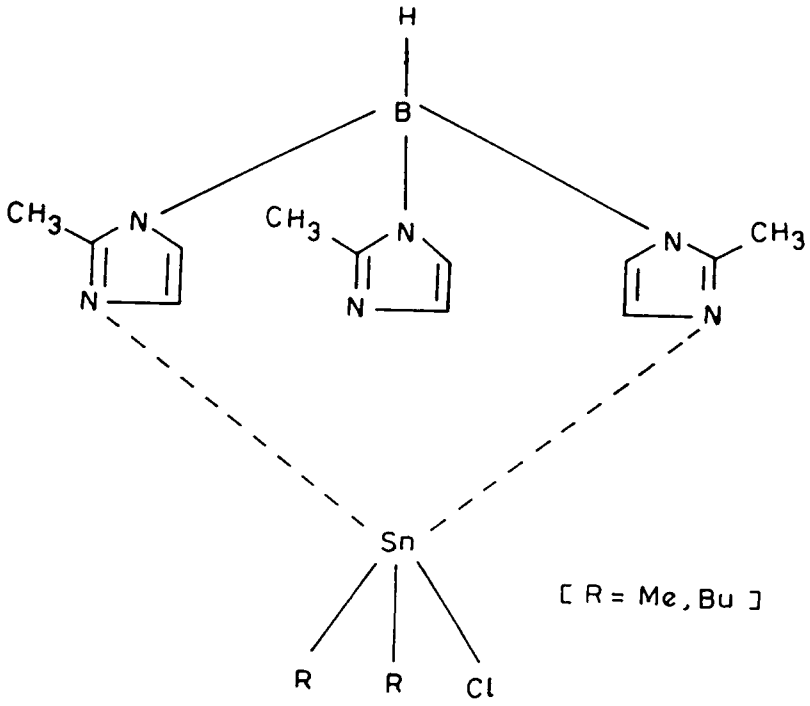
[R = Me, Bu]

FIG. 25



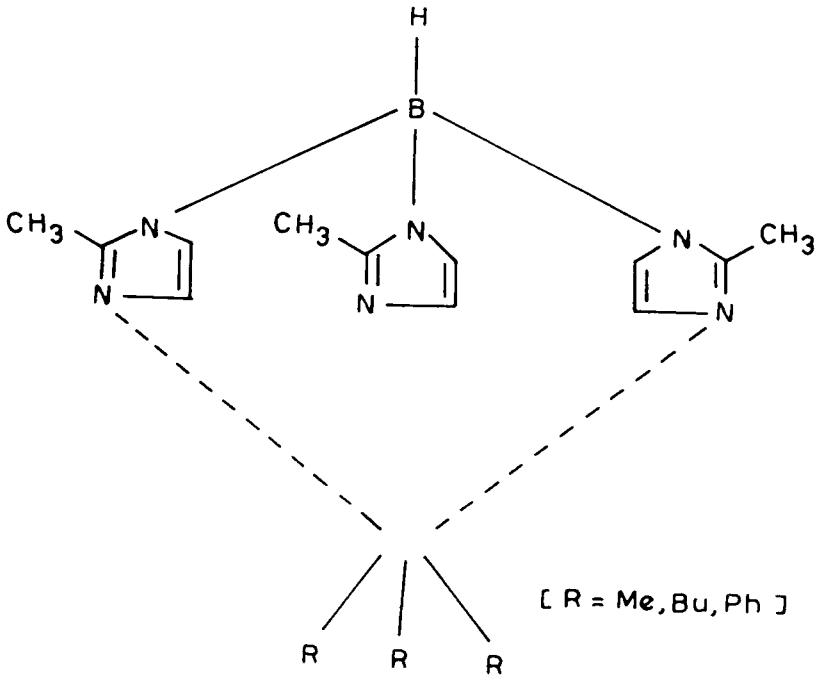
[R = Me, Bu, Ph]

FIG. 26



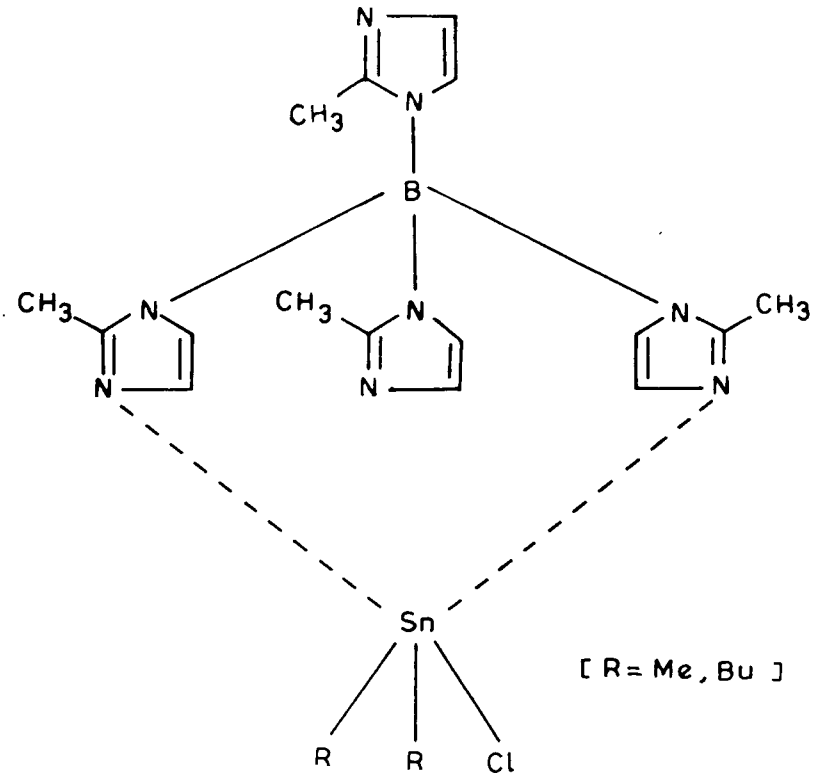
[R = Me, Bu]

FIG. 27



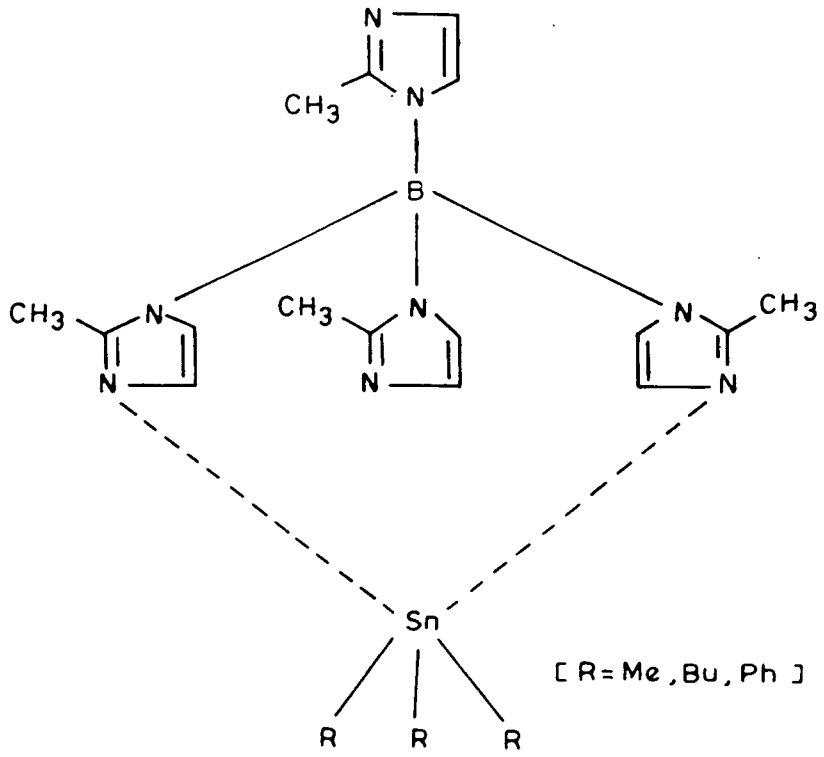
[R = Me, Bu, Ph]

FIG. 28



[R= Me, Bu]

FIG. 29



[R= Me, Bu, Ph]

FIG. 30

The peaks observed between δ 0.50-0.7, δ 0.69-2.3 and δ 7.8-8.1 ppm are assigned to the tin-methyl, tin-butyl and tin-phenyl signals respectively in all the complexes.

A square pyramidal geometry for the dihydrobis complexes and an octahedral geometry for the hydrotris and tetrakis complexes, similar to those reported for the unsubstituted analogue is proposed. The probable structures of the complexes are given in figures 25-30.

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C H A P T E R VI

THE PREPARATION AND CHARACTERIZATION OF DI- AND TRIORGANOTIN COMPLEXES OF DIHYDROBIS(INDOLYL) BORATE ANION

CHAPTER VI

THE PREPARATION AND CHARACTERIZATION OF DI- AND TRIORGANOTIN COMPLEXES OF DIHYDROBIS (INDOLYL) BORATE ANION

INTRODUCTION

Indoles and substituted indoles have been found to exhibit marked physiological activities in a number of biological process [1]. Some indoles are reported to act as anti tumor agent in mice [2], and anti inflammatory reagent in bone fracture repair in rats [3]. They also find effective uses in different skin diseases [4] and in many metabolic disorder in urine [5]. Because of their biological significances, the coordination chemistry of indoles has been subjected to extensive studies by several workers. However unlike pyrazole, indazole and imidazole, the indole has not so far been exploited for the synthesis of the new class of chelating ligand where boron may be bonded to the nitrogen atom of the indole nucleus. In extending our work on the chemistry of B-N bonded heterocycles, it was considered desirable to synthesize poly (indolyl) borate and their complexes with alkyl tin halides, with a view to examining their coordination ability towards the tin atom.

EXPERIMENTAL

Dimethyl tin chloride, dibutyl tin chloride, trimethyl

tin chloride (all Fluka), tributyl tin chloride (E. Merck), Indole (Wilson) and Potassium borohydride (BDH) were used as received.

Preparation of potassium dihydrobis (Indolyl) borate

The ligand potassium dihydrobis (Indolyl) borate was obtained by refluxing potassium borohydride 0.46 g (8.51 m mol) and indole 2 g (17.07 m mol) in a 1:2 molar ratio in dry DMF (~30 ml) for about twelve hours, when calculated amount corresponding to 2 equivalent moles of hydrogen was evolved. After the reaction was complete, the solution became dark violet. The reaction mixture on cooling to room temperature yielded a white solid which was filtered, washed and dried in vacuo.

$$KBH_4 + 2C_8H_7N \rightarrow K^+[C_{16}H_{14}N_2B]^- + KCl$$

Preparation of the complexes

Synthesis of all the complexes has been carried out by reacting the above prepared ligand with alkyltin halides in a 1:1 ratio according to the following method.

Dialkyl tin complexes

Stoichiometric amount of the ligand, potassium

dihydrobis (indolyl) borate solution in ∽ 20 ml of methanol and dimethyl tin dichloride, 1 g (4.55 m mol) or dibutyl tin dichloride, 1 g (3.29 m mol) each in 20 ml of methanol were mixed and stirred for six hours. The precipitated KCl was filtered off and the reaction mixture was refluxed for about eight hours. On standing for a week's time at 0°C, the concentrated solution yielded white crystals.

$$R_2SnCl_2 + K^+[C_{16}H_{14}N_2B]^- \rightarrow [R_2Sn(C_{16}H_{14}N_2B)Cl]$$

Where R = Methyl or butyl

Trialkyl tin complexes

A mixture of the stoichiometric amount of the ligand solution in ∽ 20 ml of methanol and trimethyl tin chloride 1 g (5.00 m mol) or tributyl tin chloride 1 g (3.0 m mol) or triphenyl tin chloride 1 g (2.59 m mol) each in ∽20 ml of methanol were stirred at room temperature for about six hours. When the KCl was filtered off, the resulting solution was refluxed for eight hours which on standing for a week at 0°C gave white solid crystals.

$$R_3SnCl + K^+[C_{16}H_{14}N_2B]^- \rightarrow [R_3Sn(C_{16}H_{14}N_2B)] + KCl$$

Where R = Methyl or butyl or phenyl

Physical measurements and analysis

The complexes were analysed for metal contents by standard procedures. Carbon, hydrogen and nitrogen were estimated by microanalytical service of the department. Infrared and far infrared spectra in KBr and Nujol mull respectively were recorded with a Perkin-Elmer spectrophotometer model 621. The ^{1}H nmr spectra (in $CDCl_3$) were recorded on a varian A-60 instrument.

RESULTSAND DISCUSSION

The ligand potassium dihydrobis (indolyl) borate used in the present investigation is a substitution product of indole and potassium borohydride taken in 2:1 stoichiometric ratio. The formation of the ligand, dihydrobis (indolyl) borate anion was ascertained by the evolution of the corresponding 2 moles of hydrogen gas during the reaction. Completion of reaction was indicated by the disappearance of N-H band in its infrared spectrum and appearance of a new sharp band of medium intensity at 1380 cm^{-1} assigned to B-N bond [6]. A doublet found around 2420-2390 cm^{-1} is a strong evidence for the existence of the B-H linkage [7,8]. The splitting of this band indicates that the two hydrogen atoms are not in the same plane which is in agreement with the tetrahedral nature of BH_4^- ion. The characteristic frequencies

of the indole molecule appear in the spectrum of the ligand at their appropriate positions and all of them retain shapes and intensities. A band in the region around 1590 cm^{-1} has been assigned to the C=N stretching frequency [9] and a band at 1610 cm^{-1} as the ring stretching frequency. The probable structure of the ligand is shown in the figure 31.

Table 7 lists the ligand and the complexes prepared along with their melting points, % yield and microanalytical data. The result of elemental analysis are consistent with the proposed composition which indicates a 1:1 metal:ligand ratio.

The band observed in the far i.r. spectra in the region 510-370 cm^{-1} are assigned as Sn-N stretching vibrations. However, the assignment of these bands are rather difficult as Sn-C stretching frequencies of the alkyl tins as well as some of the ligand vibrations also fall in the same region. In the case of dialkyl tin complexes the bands found in 240-265 cm^{-1} region are identified as Sn-Cl stretching frequencies. A marked decrease in Sn-Cl stretching frequencies after complex formation has been noticed with the increasing coordination number, an effect which agrees with a mainly ionic nature of Sn-Cl bond [10]. The stretching frequencies of tin-methyl, tin-butyl and tin-phenyl bands remain unchanged under these circumstances. A similar effect has been noted

Table 7

Analytical data for the complexes

Complexes	MP (°C)	Yield (%)	Elemental Analysis % C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	%Sn Found (Calcd)	%Cl Found (Calcd)	Molar conductance * ohm^{-1} cm^2 $moles^{-1}$
$K^+[H_2B(In)_2]^-$	286	75	68.01 (67.60)	4.87 (4.92)	3.80 (3.87)	-	-	0.003
$[H_2B(In)_2(SnMe_2Cl)]$	260	65	50.44 (50.40)	4.52 (4.66)	6.50 (6.53)	27.48 (27.53)	8.20 (8.28)	0.235
$[H_2B(In)_2(SnBu_2Cl)]$	270	62	56.00 (56.19)	6.11 (6.24)	5.28 (5.46)	23.12 (23.02)	6.88 (6.92)	0.289
$[H_2B(In)_2(SnMe_3)]$	300	60	55.80 (55.88)	5.46 (5.63)	6.92 (6.86)	28.77 (28.92)	-	0.642
$[H_2B(In)_2(SnBu_3)]$	325	58	62.77 (62.92)	7.72 (7.67)	5.12 (5.24)	21.92 (22.09)	-	0.001
$[H_2B(In)_2(SnPh_3)]$	275	61	68.60 (68.68)	4.76 (4.88)	4.66 (4.71)	19.80 (19.86)	-	0.572

*Molar conductance of 10^{-3} M solution.

Table 8

Characteristic Infrared bands for the complexes

Complexes	B-H stretching (cm^{-1})	B-N stretching (cm^{-1})	C=N stretching (cm^{-1})	Ring stretching (cm^{-1})	Sn-N stretching (cm^{-1})	Sn-Cl stretching (cm^{-1})
$K^{+}[H_2B(In)_2]^{-}$	2420	1380	1590	1610	-	-
$[H_2B(In)_2(SnMe_2Cl)]$	2410	1365	1590	1605	480	240
$[H_2B(In)_2(SnBu_2Cl)]$	2405	1370	1570	1610	510	265
$[H_2B(In)_2(SnMe_3)]$	2420	1375	1585	1600	430	-
$[H_2B(In)_2(SnBu_3)]$	2415	1385	1595	1600	370	-
$[H_2B(In)_2(SnPh_3)]$	2400	1365	1575	1610	425	-

in many other alkyl tin halide adducts [11,12]. This suggests that the Sn-C band in these compounds are relatively unaffected by change in the coordination number of the central tin atom.

The involvement of the nitrogen of the ligand in the coordination would cause a shift to lower energy in some of the ligand vibrations. However, the ligand vibrations in the i.r. spectra (Table 8) of the complexes are not much different from those in the free ligand and only small shifts are observed. A comparison of i.r. spectra of the ligand and those of complexes show a slight decrease in the C=N stretching frequencies, which may be rationalized on the basis of the fact that the C=N bond is insensitive to coordination [13], indicating the involvement of the nitrogen atom in coordination. A slight shift of the B-N stretching frequencies to lower wave number from its position in the free ligand is also observed in the i.r. spectra of the complexes. A very slight shift in BH_2 peaks upon complex formation was also noticed. To obtain more information about the stereochemistry and the mode of coordination, proton n.m.r. spectral studies were carried out.

The ^1H n.m.r. spectrum of the ligand dihydrobis (indolyl) borate anion in $CDCl_3$ exhibits signals due to α protons of the

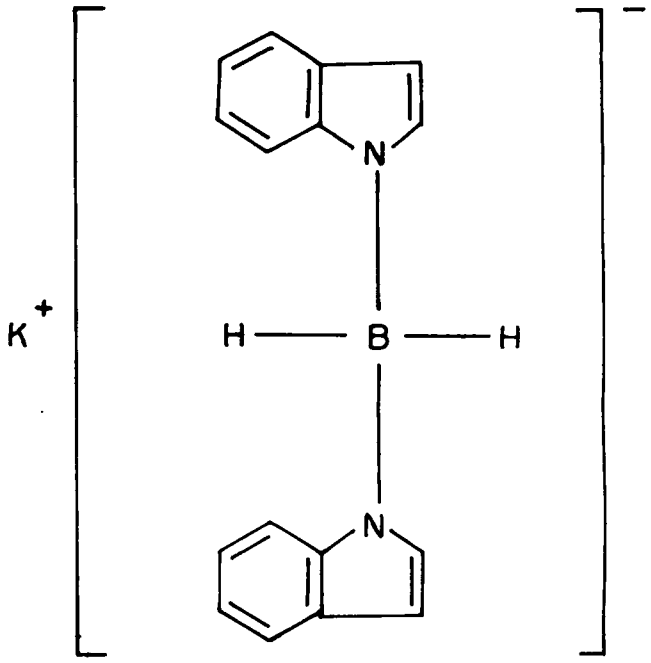

FIG. 31

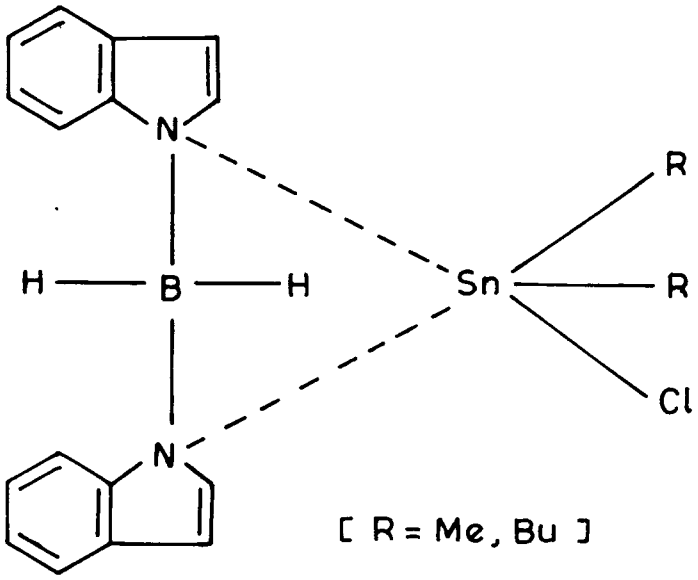

FIG. 32

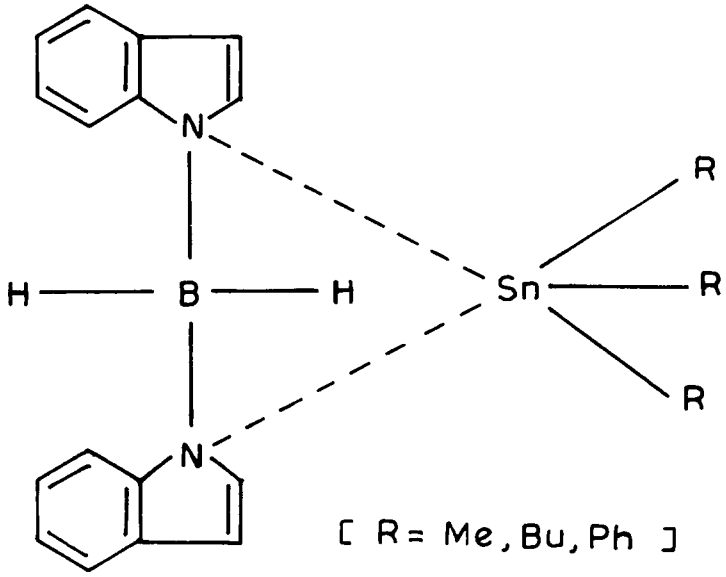

FIG. 33

indole at δ 6.67 ppm in the form of a triplet. The β proton signal which appears as triplet at higher field (δ 6.37 ppm) than in the case of α proton, lies beyond and at higher field than the absorption peaks of aromatic protons (δ 8.0 to 7.0 ppm). The nonappearance of any signal at around δ 7.1 indicates the absence of N-H band in the molecule. The signal due to boron hydrogens could not be located, probably because the resonance is broadened by interaction with the ^{11}B quadrupole (I = 3/2). On complex formation, the β and α proton signals undergo a downfield shift of about δ 0.8 to 1.32 ppm unit from the corresponding position in the free ligand probably due to the electron withdrawal by the tin atom.

The signals observed between δ 0.51-0.76, δ 0.75-2.1 and δ 8.1-8.3 ppm are assigned as tin-methyl, tin-butyl and tin-phenyl peaks respectively in all the complexes.

On the basis of the above discussion a five coordinated square pyramidal geometry for these complexes, as shown in figures 32 and 33, is proposed where the ligand coordinates in a bidentate manner.

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